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AIR RESOURCES BRANCH  
ATMOSPHERIC RESEARCH AND  
SPECIAL PROGRAMS

MONITORING OF POLYCHLORINATED  
BIPHENYLS OF STACK GAS BY  
THE MOE TAGA 3000 SYSTEM

ARB-23-82-ARSP

A Comprehensive Technical Report  
Prepared for  
Ministry of the Environment  
Air Resources Branch

by

Sciex Inc.  
55 Glen Cameron Road  
Apt. 202  
Thornhill, Ontario  
L3T 1P2



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## 1.0 SUMMARY

A methodology has been developed to monitor ambient air and stack gas for polychlorinated biphenyls (PCB) using a TAGA<sup>TM</sup>3000 unit owned by the Ministry of the Environment. This study may be divided into three phases. Phase I involves preparations of the MOE TAGA<sup>TM</sup>3000 van for the determination of PCBs in the atmospheric environment. Various hardware and software were developed and prepared during this period. Interference problems and counter measures were also dealt with during this Phase. Phase II entails stack monitoring simulation at SCIEX premises. Steam and carbon dioxide were introduced into heated outdoor air. The behavior of PCBs was examined under various conditions in order to achieve near 100% PCB transmission efficiency throughout the simulation sampling line, and a rapid system's response to added PCBs.

In Phase II efforts were concentrated on preparation of the MOE TAGA<sup>TM</sup>3000 unit for monitoring stack gas for the presence of PCBs during anticipated PCB test burns at St. Lawrence Cement Company in Mississauga, Ontario. The cement kiln slated for PCB test burns uses coal and coke. It discharges approximately 56 M<sup>3</sup>/sec of stack gas containing 41% steam by volume. The stack gas was sampled at a rate 200 ml/sec at 225°C, mixed with 1500 ml/sec of heated outdoor air to lower its dew point and to dilute for optimum analysis, and filtered with a 10-micron quartz filter. The filtered gas mixture was transferred down to the TAGA<sup>TM</sup>3000 unit through 25 m long, 2.5 cm bore, heat-traced glass line at 120°C-150°C. The sample gas was reduced to 50°C with a heat exchanger placed immediately upstream of the TAGA<sup>TM</sup> unit. The gas mixture was introduced into the TAGA<sup>TM</sup>300 corona discharge region via a wire integrator after a 2-minute sample enrichment. PCBs present in the stack gas or added to the gas mixture for calibration purposes were

highlighted by benzene charge transfer. The identification of PCBs was based on the molecular weights of 12 ion species (i.e., to isotopic peaks each for mono-through hexachlorobiphenyl), isotopic ratios and linear correlation coefficients between responses for the individual species. This technique has allowed the detection of PCBs (added to the stack gas in the sampling line) down to the level of 200 to 300 ng/m<sup>3</sup> for each of the six chlorinated species.

The transfer efficiency of the sampling line was greater than 95%. Changes in PCB concentration at the duct resulted in a rapid change at the monitor, so that within the limits of 2-minute integration, the PCB level could be monitored in real time.

Table 1.1 Minimum Detectability of PCBs

Added to Outdoor Air

PCB Species	Mono	Di	Tri	Tetra	Penta	Hexa
Mass Peak	188	222	256	292	326	362
Detectability (ng/m <sup>3</sup> )	8.1	4.2	3.9	2.4	1.8	11.1

Worst-Case Minimum Detectability (Sum of All Species) 31.5 ng/m<sup>3</sup>

The "worst-case" minimum detection limits by the MOE TAGA<sup>TM</sup>3000 have been observed to fluctuate on a day-to-day basis due to the changing and fluctuating background chemicals present in ambient air. These results indicate a need to establish the background levels of chemicals on a day-to-day basis.

Table 1.2 summarizes the minimum detectability of the vaporized PCBs

added to the stack gas in micrograms per cubic meter with a signal-to-noise ratio of 3:1. This signal-to-noise ratio is quite stringent, and during the test burn it will be possible to measure with a lower ratio.

Table 1.2 Minimum Detectability of PCB

Added to Stack Gas

PCB Species	Mono	Di	Tri	Tetra	Penta	Hexa
Mass Peak	188	224	256	290	324	360
Detectability (ug/m <sup>3</sup> )	2.335	2.443	0.392	1.671	0.571	1.109

Worst-case Minimum Detectability (Sum of All Species) 9.251 ug/m<sup>3</sup>)

These detection limits were also found to fluctuate on a day-to-day basis. However, none of these minimum detection limits exceeds the safety limit of 20 micrograms per cubic meter specified in the Test Protocol (Ref. 5).

Correlation coefficients between (a) the equivalent concentration and total system's response were in the range of 0.928 to 0.996, and (b) the responses of the two most abundant isotopes of each PCB group were between 0.980 and 0.999. The deviation between the observed and theoretical (or expected) isotopic ratios are within 5% except for hexachloro species (11%). These correlations lead to an added confidence in distinguishing between a true PCB response and interfering background peaks. This can be further substantiated by the poor correlations (0.1 - 0.4) when PCBs were not added to outdoor air or to the diluted stack gas.

## 2.0 INTRODUCTION

### 2.1 Scope of This Report

This technical report has been prepared to describe experimental aspects of the development for the analysis of polychlorinated biphenyls present in ambient air and possibly in stack gas during a PCB test incineration using a mobile TAGA<sup>TM</sup>3000 air monitor owned by the Ontario Ministry of the Environment (hereinafter called the Ministry). This report has been designed to meet the needs most likely to be experienced by TAGA<sup>TM</sup>3000 users for the determination of PCBs in the atmospheric environment and in process gases, such as industrial waste incineration. As such it is assumed that the reader is familiar with common knowledge and procedures practiced in the environmental analytical laboratories, e.g., preparation of standard solutions, use of microsyringes, calibration curves, basic statistics, chemical symbols and so on. It has been also assumed that detailed explanations on the TAGA<sup>TM</sup>3000 electronics, thermodynamics, complex reaction kinetics, computer programming and other advanced, but peripheral matters are beyond the scope of this report.

In order to make this report as cohesive and instructive as possible, we have included observations, experiences, materials and information obtained not only from the work carried out on behalf of the Ministry but also from various studies generated internally at SCIEX INC., or assignments carried out on behalf of several clients.

Most of the work described in this report was done under trying

circumstances; the air monitor had been assembled when this program was initiated. The instrument required a number of modifications. Computer programs had to be upgraded continuously. Data were often collected under different conditions; therefore, they may not be comparable in a strict sense.

Thus, this report will present how experiments have been carried out, and for what reasons, rather than trying to draw definite conclusions from data produced under continuously advancing development conditions. Also because of very limits time or budget allowances, certain experiments were conducted in haste, resulting in inconclusive observations. If certain experiments are desired to be repeated, these will be mentioned in this report so that the reader can reproduce those experiments to confirm our observations.

## 2.2 Background

Polychlorinated biphenyls (PCBs) are a class of chlorinated aromatic compounds, and have been one of the most controversial environmental issues since the 1966 discovery of the widespread occurrence of these chemicals in the Swedish environment (Ref. 1).

Because of their excellent chemical and physical properties PCBs had been used in various fields such as electric capacitors, transformers, hydraulic fluids, vacuum pump oil and plasticizers.

PCBs have been found to cause skin disorders (chlorance), birth defects, nervous disorder, degeneration of the liver and cancer. Because of their lipophilic nature PCBs accumulate in living matter through the food chain.



It is estimated that approximately 14 metric kilotons of PCBs are awaiting disposal and 18 kilotons of PCBs are still in use in Canada in electrical equipment (Ref. 2). Due to their toxic and persistent nature PCBs pose a serious disposal problem. Land fill and incineration have been the most common disposal methods for toxic wastes. Deep welling and other similar methods of land disposal are enviornmentally unsound, as dramatically demonstrated in Love Canal, Niagara Falls, New York (Ref. 3). The incineration method is more attractive and final than any other method of disposal. For PCBs, incineration in a cement kiln has the following distinct advantages over normal incinerators:

- (1) In cement manufacture, the kiln operates at higher temperatures and for longer residence times than those used in common industrial waste incinerators.
- (2) It is a common practice in the cement industry to add chlorides to the kiln to reduce the alkali content of the final product. The use of PCB wastes in a cement kiln would provide useful recovery of chlorine and energy, and at the same time, solve a serious disposal problem.

In order to examine whether this incineration method would cause any adverse air pollution, experimental work was carried out on the Burning of PCBs in the NO. 1 kiln at St. Lawrence Cement Company in Mississauga, Ontario in the late 1975 to the early 1976 (Ref. 4).

The above tests have shown virtually complete destruction of the PCBs at feed rates of between 0.5 and 5.7 kg/min. The sampling and

analytical methods used for emission testing at the time were too insensitive to detect low concentrations of PCBs in the effluent gas stream. The stack gas concentrations of PCBs were less than 160 ug/m<sup>3</sup> and probably less than 3 ug/m<sup>3</sup>. The analytical and sampling techniques available at the time for the trial were inadequate to detect many of the possible emissions unless sampling durations were excessively prolonged (Ref. 5).

In order to achieve improved analytical capabilities, and faster detection and quantitation of PCBs, a program was proposed by the Ministry of the Environment to achieve the above goals using the MOE TAGA<sup>TM</sup>3000 unit (TAGA = Trace Atmospheric Gas Analyzer).

## 2.3 Goals

### 2.3.1 Phase I (March 1979 - May 1979): Preparations of the MOE TAGA<sup>TM</sup>3000 van for the determination of PCBs in the atmospheric environment.

At the beginning of this Phase the MOE TAGA<sup>TM</sup>3000 van had just been assembled and was not ready to monitor ambient air for PCBs.

Therefore, the main objectives for this Phase were as follows:

2.3.1.1 To make the newly assembled MOE TAGA<sup>TM</sup>3000 unit compatible with ambient air PCB monitoring.

2.3.1.2 To transfer the ambient air PCB analysis technology developed on the TAGA<sup>TM</sup>2000 system (Ref. 6) to the MOE TAGA<sup>TM</sup>3000 unit.

2.3.1.3 To develop a fast repetitive peak jumping method to monitor a number of PCB species of interest at each adsorption/desorption cycle.

2.3.1.4 To develop methods to reduce interference from chemical noise, or to separate PCB signals from the interfering signals.

Some of these tasks were too complex to solve within the time limit of this Phase and continued throughout this program.

2.3.2 Phase II (June 1979 - August 1979) Stack Monitoring Simulation.

It had been decided to use the TAGA<sup>TM</sup>3000 unit to monitor possible PCBs in the stack gas discharged from kiln No. 1 during a test burn, as described in the Test Protocol (Ref. 5). There were two main objectives assigned for this Phase.

2.3.1 To provide a gas source which matched as closely as possible the stack gas composition, together with an experimental sampling system to permit various approaches to PCB transfer into the TAGA<sup>TM</sup> system.

2.3.2.2 To measure all the pertinent PCB transfer characteristics of the most promising approaches tried, in order to assess the feasibility of achieving the required analytical capability and to provide the basic design inputs for the total system to be installed on the St. Lawrence Cement stack system.

2.3.3 Phase III (August 1979 to May 1980).

In this Phase the MOE TAGA<sup>TM</sup>3000 van was stationed at the St.

Lawrence Cement Plant in Mississauga. Except for the significant interruption due to the monitoring of spills as a result of Canadian Pacific Railway's Derailment and subsequent van maintenance, most of the work was carried out at the St. Lawrence Cement Plant. The main objectives for this Phase were:

2.3.3.1 To design and install a stack sampling system appropriately connected to the MOE TAGA<sup>TM</sup>3000 unit, based on the best design information resulting from the simulation study carried out at SCIEX premises.

2.3.3.2 To run preparatory tests to study any effect not covered in the simulation, notably the effects of dust, stack depression below ambient pressure, and concomitant combustion products in the stack gas.

2.3.3.3 To document the overall response characteristics (sensitivity, response time and minimum detectability limits) for the total system using known PCB concentrations obtained by known PCB injections at the head of the sampling line.

## 2.4 Tasks

In order to achieve the above mentioned goals the following major tasks were assigned by the Ministry of the Environment and carried out by SCIEX INC. in co-operation with Ministry personnel and St. Lawrence Cement staff.

### 2.4.1 Tasks given during Phase I (March 1979 to May 1979)

#### 2.4.1.1 Design and Installation of PCB Analysis Hardware

In order to make the MOE TAGA<sup>TM</sup>3000 system capable of ambient air PCB analysis, design, manufacture and install the following items:

- (a) PCB wire integrator assembly including supporting brackets, sample flow and temperature measuring devices.
- (b) Benzene chemical ionization reagent delivery system consisting of a cylinder of prepurified air, pressure valves, gauges, molecular sieve purification train, gas distribution manifold, metering valves, rotameters, gas bubbling bottle, stand, tubes and Swagelok fittings.
- (c) Variable DC power supply with an ampere meter, switch, box and necessary wires etc. to power the PCB wire integrator for thermal desorption. In the past a variable transformer had been used; however, it was found that the AC power supply interfered with the operation of the TAGA software, possibly due to some induction effects.
- (d) Charcoal filters to trap the PCBs which have been introduced into the TAGA<sup>TM</sup>3000 flow system for calibration purposes.

2.4.1.2 Transfer of the TAGA<sup>TM</sup>2000 Technology for the Determination of PCBs in ambient air to the MOE TAGA<sup>TM</sup>3000 system. This involves adsorbent coating, optimization of adsorption and thermal desorption cycles by varying the length and temperature of sample adsorption, sample flow rate, heating profile and other subtle parameters pertinent to the PCB analysis.

#### 2.4.1.3 Fast Repetitive Peak Jumping Method.

In the method developed on the TAGA<sup>TM</sup>200 system (Ref. 6) the instrument was not equipped with an advanced computer system. Consequently, each adsorption/desorption cycle could produce a mass spectral response at only one fixed mass-to-charge ratio of interest. Although the signal generated in this way was large, this method was very time consuming in comparison to the current method which gives responses at 12 peaks of interest per each adsorption/desorption cycle.

This task, therefore, involved the development and trail of new computer programs, DSORBA PCONCA and PCBMON. This tasks has been one of the most difficult assignments carried out during the whole study. Because of its size and complexity this task spanned over the subsequent phases. At the end, this continuous effort produced the most effective means to separate PCB signals from the interfering chemical noises, and to gather and reduce a large volume of information.

The computerization also necessitated the development of special signal handling circuit board.

#### 2.4.1.4 Extraction of PCB Signals from Interfering Chemical Noises.

At the beginning of this Phase a serious interference problem was experienced due to automotive exhaust and other chemicals present in ambient air. This task was initiated to reduce these noises and to extract two PCB signals from total signals by the following techniques:

- (a) Measurement of responses at the two most abundant isotope peaks for each biphenyl species substituted with an identical

number of chlorine atoms, followed by the comparison of their ratio to their theoretical isotopic ratio.

- (b) Evaluation of linear correlation coefficients between the TAGA<sup>TM</sup>3000 responses to the two most abundant isotopes of each group of PCBs containing the same number of chlorine atoms.
- (c) Evaluation of linear correlation coefficients between the system response and equivalent concentration produced by adding a known amount of PCB standards to a known flow of the TAGA<sup>TM</sup> carrier gas.
- (d) Evaluation of linear correlation coefficients between responses at various mass-to-charge ratios covering monochlorobiphenyl through hexachlorobiphenyl, e.g., responses at  $m/z = 188$   $m/z = 256$  vs  $m/z = 360$ .
- (e) Careful selection of lens voltages (L1-L5), rod offset, resolution at each  $m/z$  of the 12 PCB peaks of interest.
- (f) Optimization of the start and end of the PCB signal integration at each  $m/z$  position of interest to discriminate against interfering chemical noises.
- (g) Use of chemical filters such as activated charcoal and Florisil to prepare organic-free carrier air for calibration purposes.

2.4.1.5 Examination of Quality Assurance Samples.

A number of quality assurance samples were given by the Ministry, and the system's responses to some of these samples agreed well with the calculated values.

2.4.1.6 Preparation of calibration curves and Determination of Detection Limits, etc. Prepare calibration curves by adding to the system different concentrations of PCBs and calculate detection limits and sensitivities.

Because of the complex nature of these problems some of the tasks assigned in this Phase, notably the computer-oriented assignments, were undertaken throughout the entire program.

2.4.2 Tasks Given During Phase II (June 1979 to August 1979) Stack Monitoring Simulation.

2.4.2.1 Design and Installation of Stack Simulation Line.

A stack simulation line was designed and installed to provide a gas source which would approximate the stack gas composition as closely and economically as possible. This experimental sampling line also enabled various approaches to PCB transfer into the MOE TAGA<sup>TM</sup>3000 system. This simulation line consisted of a steam kettle, heat-traced borosilicate glass tubes, electric power supply to heat these tubes, a heat exchanger, heated glass injectors, a water collection system, a circulating constant temperature bath to keep the heat exchanger in the optimum temperature range, a carbon dioxide gas supply, temperature measuring devices and other necessary small pieces.



#### 2.4.2.2 Examination of Balston Type 30/25 Filter Unit.

In order to examine the thermal behavior of a Balston Type 30/25 filter unit (consisting of a Type 304 stainless steel housing, fiber glass filter and a Viton O-ring) for possible dust separation at the St. Lawrence Cement plant, a unit was installed in line with this stack simulation line and heated with heating wires to examine its thermal stability.

#### 2.4.3 Optimization of Heat Exchanger.

During the early stage of this Phase it was found that the PCB wire integrator could not adsorb PCBs in the presence of hot steam. A condenser, or heat exchanger, was used to remove the excess amount of steam from the simulation gas, and to transfer the added PCBs into the TAGA<sup>TM</sup>3000 system without serious PCB loss. The operation of the heat exchanger was optimized along with the temperature of a transfer line from the end of the heat exchanger to the PCB wire integrator.

#### 2.4.2.4 Preparation of Calibration Curves, System's Response Time, and Determination of Detection Limits and Sensitivities.

It was considered necessary to obtain information on PCB transfer efficiencies and system's response to the PCBs. A solution containing PCBs was injected at several fixed rates into the sampling line through several different injection ports to investigate transfer characteristics.

#### 2.4.3 Tasks Given During Phase III.

(August 1979 to May 1980). Stack Monitoring.

2.4.3.1 Assistance to MOE Staff in the Installation of Sampling Line.

The installation of an all glass sampling line had been initiated by the Source Testing Unit of the Air Resources Branch in late July. Our tasks involved the completion of the sampling line, especially from a complex condensation system and associated valve and by-pass assembly mounted on a plant wall to the TAGA<sup>TM</sup>3000 unit; leak testing of the entire line, line cleaning, modification and maintenance of the sampling line.

2.4.3.2 Examination of Various Filters.

Preliminary experiments had indicated serious problems associated with un-filtered stack gas in transporting PCBs through the sampling line and in detecting them. Various filtering media were investigated to obtain best dust removal without seriously affecting the operating sampling line pressure and PCB transmission through the filter. These included a wad of glass wool, a small sintered disc, filter paper and quartz cylindrical filters in several dimensions and pore sizes. Dust and water samples were collected for GC analysis.

2.4.3.3 Dilution of Stack Gas.

The stack gas had been found to contain a large amount of interfering chemicals. It was then decided to dilute the stack gas with heated ambient air. This work involved the installation of a heated ambient air line, the optimization of dilution ratio, temperature of the dilution gas and the position of dilution gas mixing.

2.4.3.4 Preparation of Calibration Curves, System Response and Determination of Detection Limits, Sensitivities and Linear Correlation coefficients.

After the selection of the best sampling line configuration and the optimization of the operating conditions of the total system, a number of injections of a standard PCB solution were made to determine the total system's responses, detection limits, background fluctuation, quality of data by linear correlation coefficients and other important pieces of information necessary to carry out a possible PCB test burn.

#### 2.4.3.5 Examination of Chemical Species and their Relationship with Kiln Operating Conditions.

In order to elucidate the nature of the chemical noises, a series of mass spectra were obtained under the normal kiln operating conditions. A comparison was also made by acquiring mass spectra while the kiln was being operated with 2.5% excess oxygen.

### 3.0 MONITORING INSTRUMENTATION \_ TAGA<sup>TM</sup>3000

#### 3.1 Atmospheric Pressure Chemical Ionization Mass Spectrometry (APCI-MS)

##### 3.1.1 - Comparision of Chemical Ionization to Electron Impact Ionization

The TAGA<sup>TM</sup> techique is based on the use of mass spectrometry to identify and quantify trace quantities of chemicals present in complex matrices, such as ambient air, process gases, biochemical specimens, organic solutions or acid extracts (for the newly developed elemental analysis front end). In order to make this analysis practical for trace chemicals in the parts-per-million to sub-parts per-trillion concentration range, a high degree of preseparation or preselection of the sample molecules or elements from the mixture must take place before mass analysis. In conventional mass spectrometry, this is achieved by passing the

sample through a gas chromatograph or a high pressure liquid chromatograph attached in series to a mass spectrometer (GC/MS or HPLC/MS). A combination of a HPLC and GC is also used to isolate chemicals from very complex mixtures. However, these techniques suffer several drawbacks:

- (a) The samples often require length work-up such as sample collection, clean-up, and concentration before HPLC or GC injection, or derivatization so that they can be eluted from the GC.
- (b) Because of the multi-step operation and of the high energy ionization practiced with conventional electron impact (EI) mass spectrometry, the detectability for trace chemicals is poor, when compared to detection limits obtained by APCI-MS.
- (c) The loss of sensitivity experienced by the conventional GC/MS or HPLC/MS can be attributed to the need for interfacing a GC or HPLC to an MS that operates at different pressures. Commonly used devices such as glass jet, silicone membrane, Watson-Biemann effusive separators for GC/MS; belt and capillary split tube for THLC MS do not allow a 100% sample transmission.

These drawbacks can result in a substantial lag time from the initial sampling to the final analysis, thus making certain analyses impractical. These include plume tracking, process

monitoring and monitoring of accidental spills, etc., where fast analysis is the necessity.

In this Report the analysis of metals will not be discussed in detail although spark source mass spectrometry has been used to analyze elements for a number of years.

The two major methods of ionization in GC/MS and HPLC/MS and electron impact (EI) and chemical ionization (CI). Chemical ionization, as the name implies, uses ion molecule reactions to ionize the compounds of interest rather than the direct primary ionization of typically 70-150 eV in EI/MS. In the conventional CI/MS, the sample is introduced into 0.5 to 1 torr of reactant gas such as methane, isobutane, and ammonia. This reactant gas is chosen so that after the initial ionization, the ion-molecule chemistry provides only a few product ions. A typical EI spectrum (75 eV) of acetic acid is compared with the CI spectrum with isobutane as a reagent gas in Figure 3.1. (Ref. 7). This figure was drawn assuming the total number of ions is the same for both EI and CI/MS (this, in fact, is not true, as is discussed in the following paragraph). The advantage of having nearly all the ionization present in one peak means a high degree of sensitivity. In EI, the small peaks representing fragments of the sample molecule would be lost in the chemical noise.

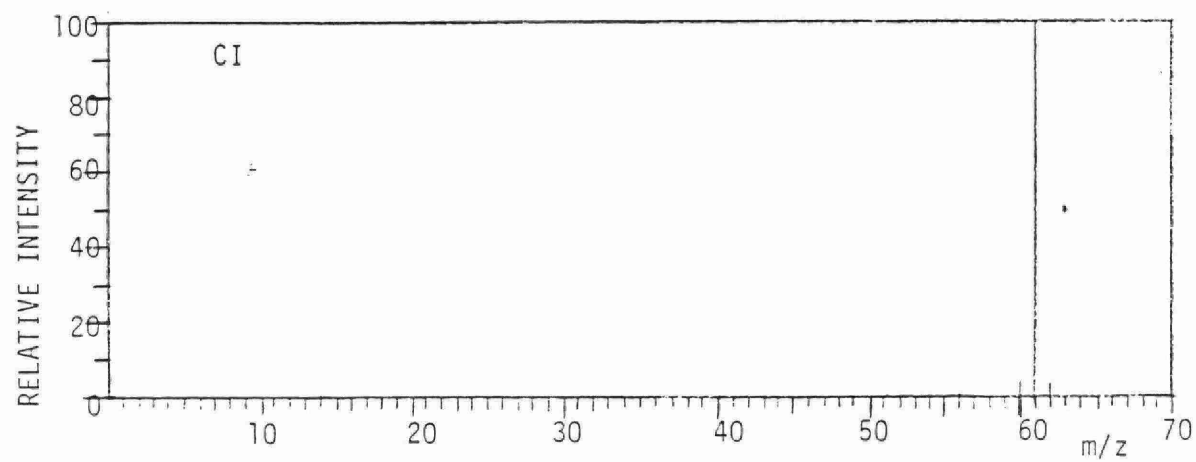
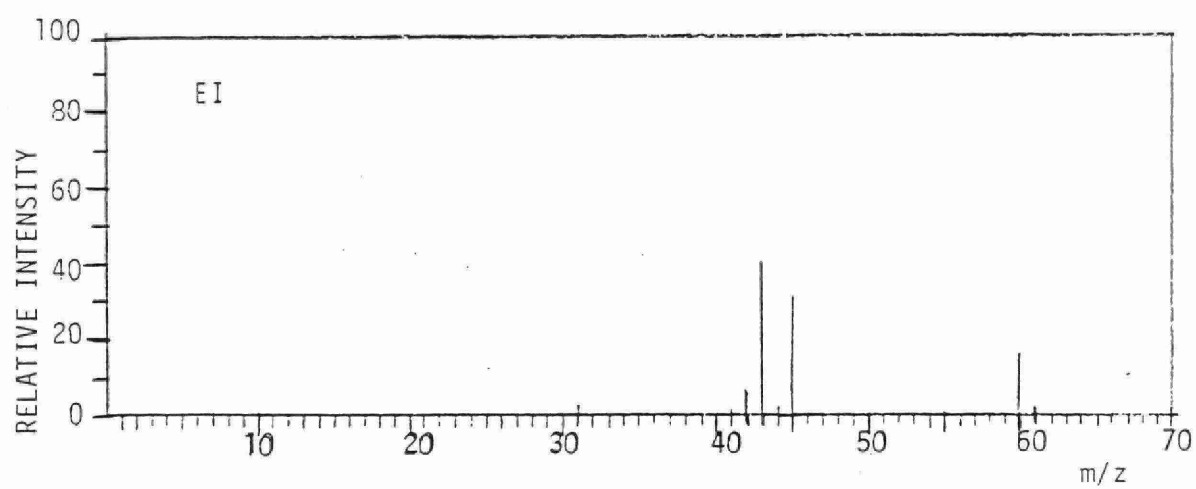
Another advantage of CI over EI is the higher ionization efficiency at the high pressures used in CI. This increase in ionization efficiency results in an increase of about two orders of magnitude in sensitivity for CI over EI/MS, when the CI source is operated at 0.5 to 1 torr.

This sensitivity improvement is even greater when the pressure in the ion source of the MS is raised to atmospheric pressure, because the increased pressure means that there are more collisions of sample molecules with reactant ions. It is this technique which enables the TAGA<sup>TM</sup> to detect trace chemicals at the ppb to sub-ppt level. In addition to the above mentioned features the TAGA<sup>TM</sup>3000 system utilizes a high-speed cryogenic pumping system to allow a relatively high throughput of the ions into the vacuum region where the ions are analyzed and detected. Other additional features are discussed in detail in Operator's Manual TAGA<sup>TM</sup>3000: TS300001 (Ref. 7).

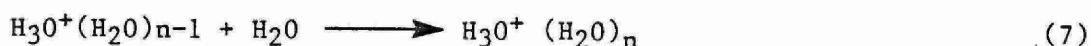
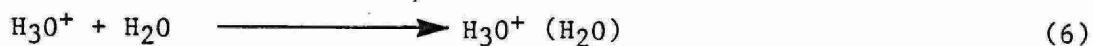
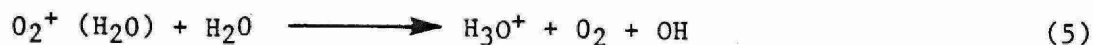
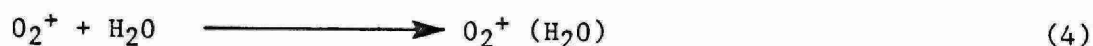
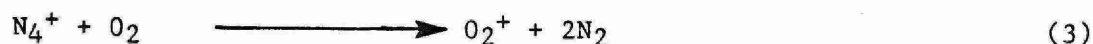
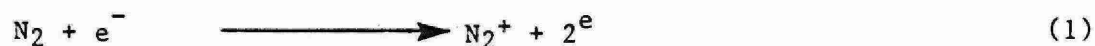
### 3.1.2 Positive Reactant Ions in Ambient Air APCI.

Atmospheric pressure chemical ionization (APCI) makes use of ion molecule chemistry for rapid, preferential ionization of trace gas molecules. In ambient air analysis, the time between sampling and analysis is instantaneous (less than one second), giving the TAGA user a "real time" display of the trace compounds present in the sample mixture. Previously collected samples are also readily analyzed with minimum workup, i.e. no chemical derivatization, using various techniques to optimize sensitivity towards particular trace compounds or trace compound classes.

FIGURE 3.1 EI & CI SPECTRA OF ACETIC ACID



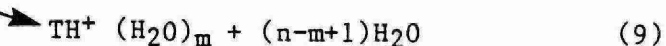
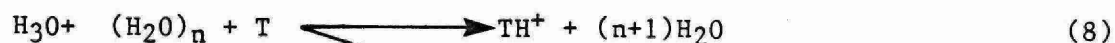
In APCI, the ionization process is initiated by electrons created in a corona discharge. The primary ions formed in the area of the discharge undergo ion molecule reactions to form a series of reactant ions. In ambient air, a simplified reaction sequence for positive ions is as follows:



The initial ionization is represented by reaction (1), where an electron removes a second electron from nitrogen, forming  $\text{N}_2^+$ . The molecular nitrogen ion then condenses with nitrogen molecules to form  $\text{N}_4^+$  (see Sections 1.4.3 and 1.4.4 of Ref. 8 for a more comprehensive discussion of ion-molecule reactions). The  $\text{N}_4^+$  ion then undergoes a dissociative charge transfer reaction with oxygen, reaction (3), to form  $\text{O}_2^+$ . This ion, in turn, condenses with a water molecule (always present in air) to form



the  $O_2^+ (H_2O)$  cluster. At this point an unusual reaction takes place with the further condensation of a water molecule with the  $O_2^+ (H_2O)$  ion. A proton hydrate,  $H_3O^+$  (equivalent to  $H^+ (H_2O)$ ), is formed. This ion then clusters with other water molecules forming a series of proton hydrates,  $H_3O^+ (H_2O)_n$ . At atmospheric pressure in the positive mode, the proton hydrates dominate the total ion spectrum within  $1 \times 10^{-6}$  seconds after the initial ionization and are the ions most likely to react with trace compounds or are the reactant ions as shown in reactions (8) and (9).

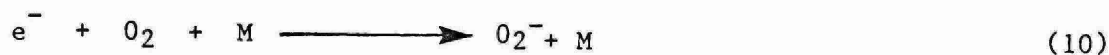


where T represents a trace compound.

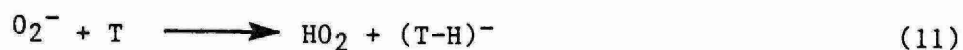
Reaction (8) represents a proton being transferred from the proton hydrates to a trace molecule, whereas in reaction (9) a proton as well as some water molecules are transferred.

### 3.1.3 Negative Reactant Ions in Ambient Air APCI

In the negative mode, electrons created by the corona discharge are rapidly thermalized (i.e. lose excess energy) through collisions with neutrals and are susceptible to electron capture reactions.



M represents a third body which aids in the release of the energy of exothermic (energy releasing) reactions such as reaction (10). The  $O_2^-$  ion and its hydrates, formed by clustering reactions with water, are the main reactant ions in the negative mode.



proton transfer



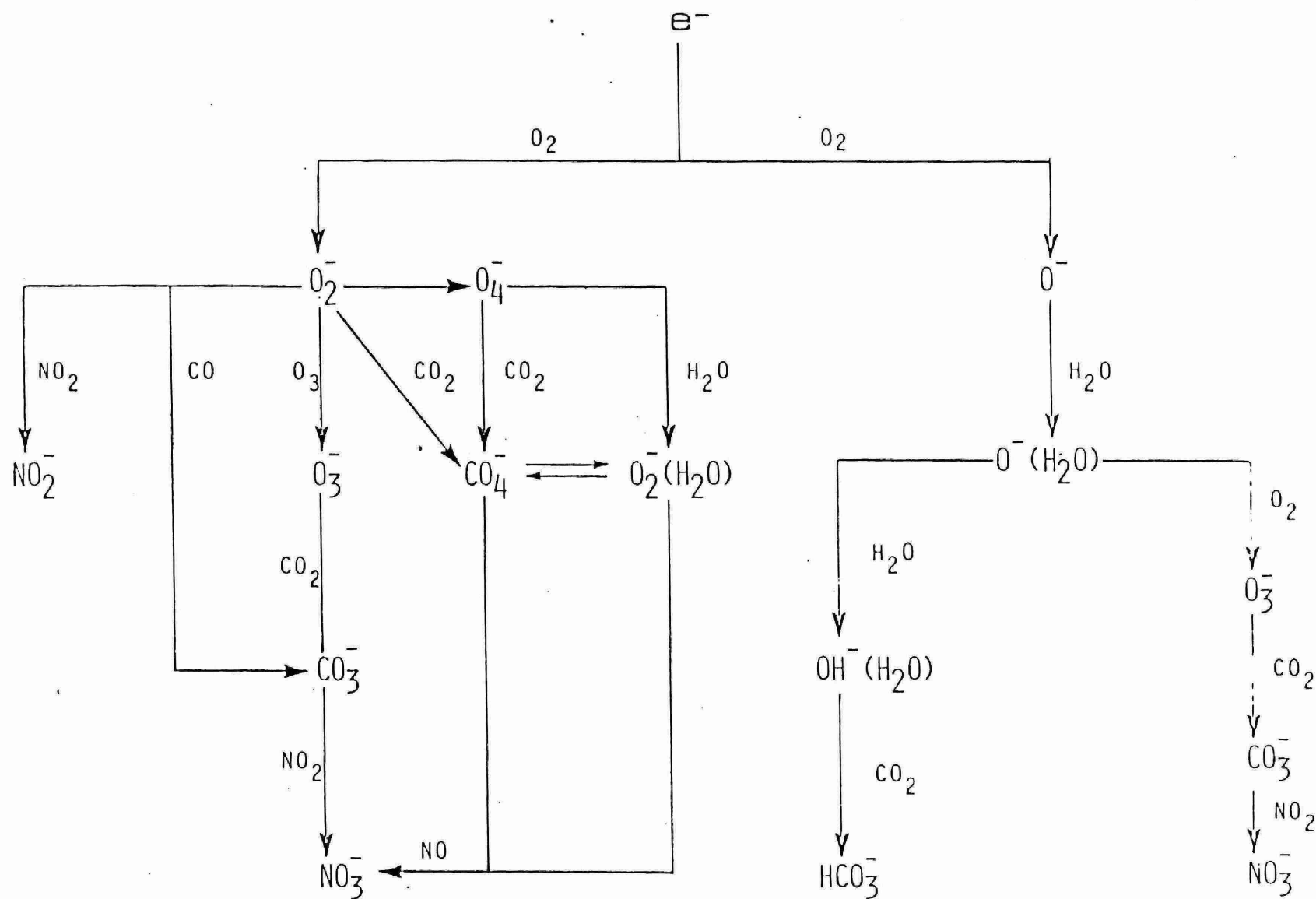
electron transfer

The complete reaction scheme for the formation of reactant ions in the negative mode is shown in Figure 3.2. The initial ionization involves electron capture and dissociative electron capture by  $O_2$ . The mechanism then becomes more complex due to the formation of a series of radicals and neutrals in the corona discharge region. These lead to the formation of a series of very stable ions:  $NO_2^-$ ,  $O_3^-$ ,  $HCO_3^-$  and  $NO_3^-$ .

However, it is  $O_2^-$  and its clusters ( $O_4^-$  and  $O_2^-(H_2O)_n$ ), which are the main reactant ions in trace analysis.

#### 3.1.4 Modifying the Reagent Ions to Detect PCBs in APCI/MS.

Due to the chemical nature of the reactant ions in both positive and negative modes in APCI/MS only certain classes of compounds can be detected at trace levels. The positive mode is governed by proton transfer reactions from the proton hydrates; the negative mode by charge transfer from  $O_2^-$  and its hydrates. In the positive mode charge transfer



NEGATIVE ION REACTION MECHANISM TO FORM  
APCI REACTANT IONS

Figure 3.2

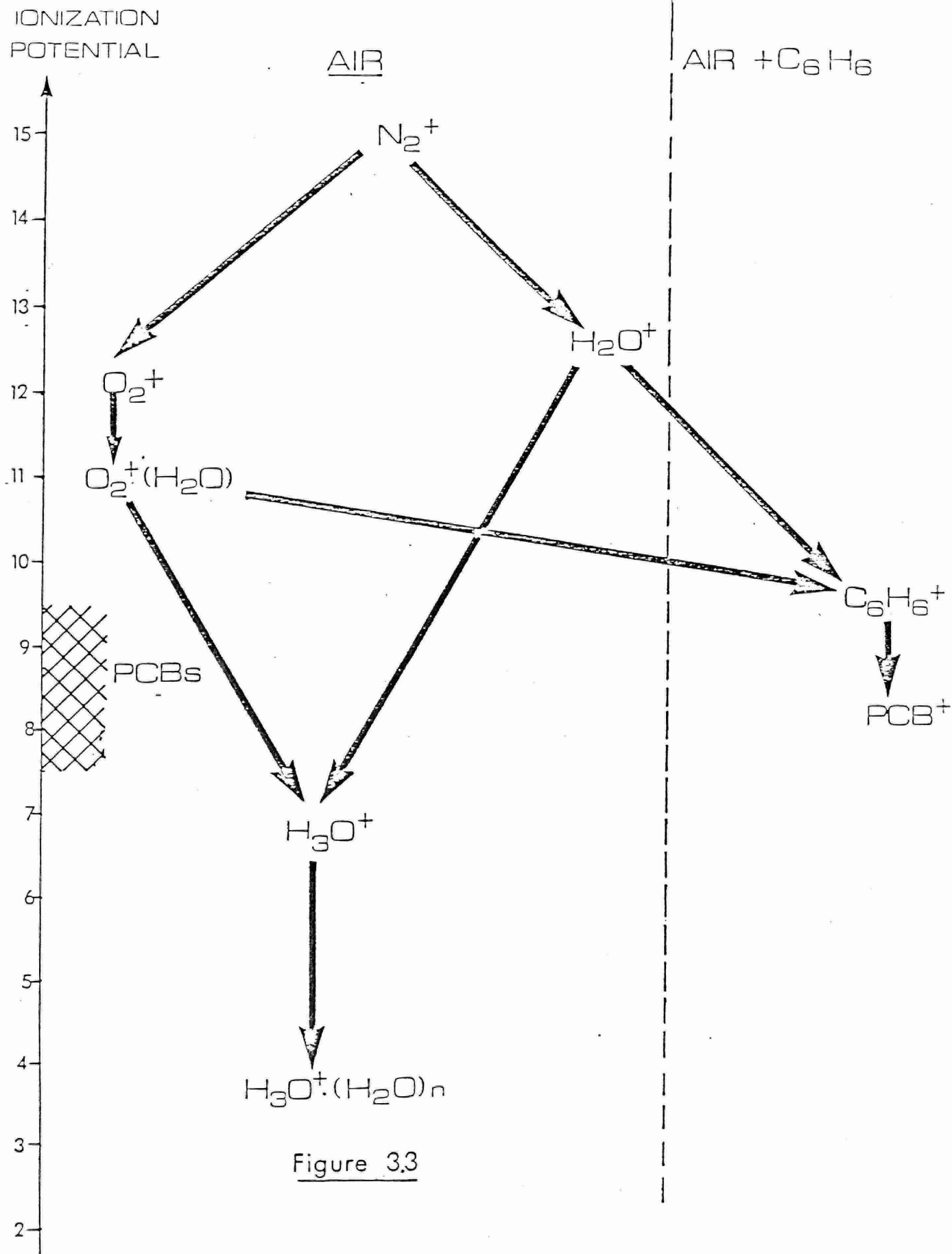
from the proton hydrate ions to the trace is highly unlikely for most compounds, since the ionization potential (IP) of most organic compounds is greater than 7 eV (160 kcal/mole) and the ionization potential of the neutral corresponding to the lowest proton hydrate,  $\text{H}_3\text{O}^+$ , is 6.44 eV. Higher hydrates,  $\text{H}_3\text{O}^+_n$  would have even lower IPs. For charge transfer reactions to occur the IP of the neutral corresponding to reactant ion must be greater than that of the trace.

On the other hand, proton transfer reactions are highly probable with proton hydrates. Protonated water clusters will pass protons to any organic compound which has a higher proton affinity (PA) than that of water clusters,  $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$ . During the development of methodologies for the analysis of PCBs described in Reference 6, PCBs were added to ambient air. No protonation was observed, and this observation plus our experimental results on chlorinated benzenes leads to the conclusion that PCBs have lower PAs than those of water clusters.

In the negative APCI mode the electron affinity (EA) of  $\text{O}_2$  and the gas phase acidity of hydrogen superoxide,  $\text{HO}_2$ , govern ion/molecule reactions. For  $\text{O}_2$  to charge transfer to a trace chemical, the trace must have a higher electron affinity than  $\text{O}_2$ . In order that proton transfer take place in the negative mode  $\text{O}_2^-$  must be able to abstract a proton from a stronger gas phase acid than  $\text{HO}_2$ .

During the methodology development (Ref. 6) the phenoxide ions were observed when PCBs were added to dry prepurified air. However, their responses were very small. No response was observed when PCB-containing

# INTERRUPTION of PROTON HYDRATE FORMATION By CHARGE TRANSFER to BENZENE



ambient air was directly introduced into the TAGA corona discharge region.

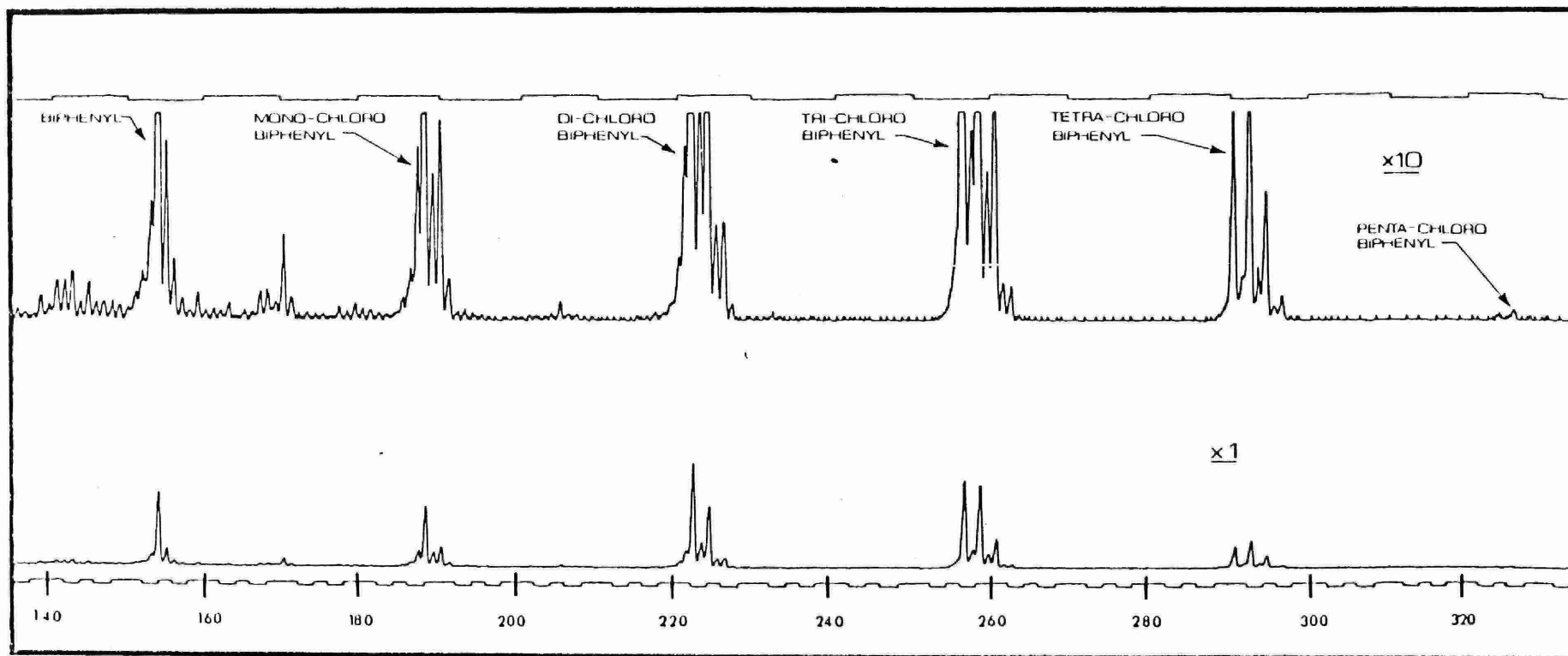
For these reasons a series of charge transfer reagents were investigated to interrupt the formation of proton hydrates. These included benzene (IP = 9.3 eV), toluene (IP = 8.82 eV), naphthalene (IP = 10.0 eV). Benzene gave the best sensitivity for the PCBs. This phenomenon can be schematically shown in Figure 3.3. The molecular benzene cation,  $C_6H_6^+$ , is relatively inert with respect to proton transfer, but will charge transfer to compounds with lower IP. The ionization boundary now becomes the IP of benzene rather than that of the proton hydrates.

Pesticide grade benzene was added to the system by passing pre-purified air through a flask containing the benzene, and adding the benzene vapor to the sample flow far enough upstream to mix completely with the carrier before it reaches the corona discharge needle. Figure 3.4 shows a mass spectrum obtained by placing a glass tube coated with Aroclor 1248 in the sampling line.

#### 3.1.5 Brief Description of the MOE TAGA<sup>TM</sup>3000 System.

The MOE TAGA<sup>TM</sup>3000 system was designed to meet many applications, and was, therefore, created in modular form. The following describes as an example, the MOE TAGA<sup>TM</sup>3000 unit equipped with an Ambient Air Analysis Front End.

As shown in Figure 3.5 the unit is equipped with a computer system comprised of a 28 K microprocessor with dual floppy disk memory, controlled from a keyboard using hard copy and graphic display units as



DETECTION OF PCBs IN AIR (AROCOR 1248)

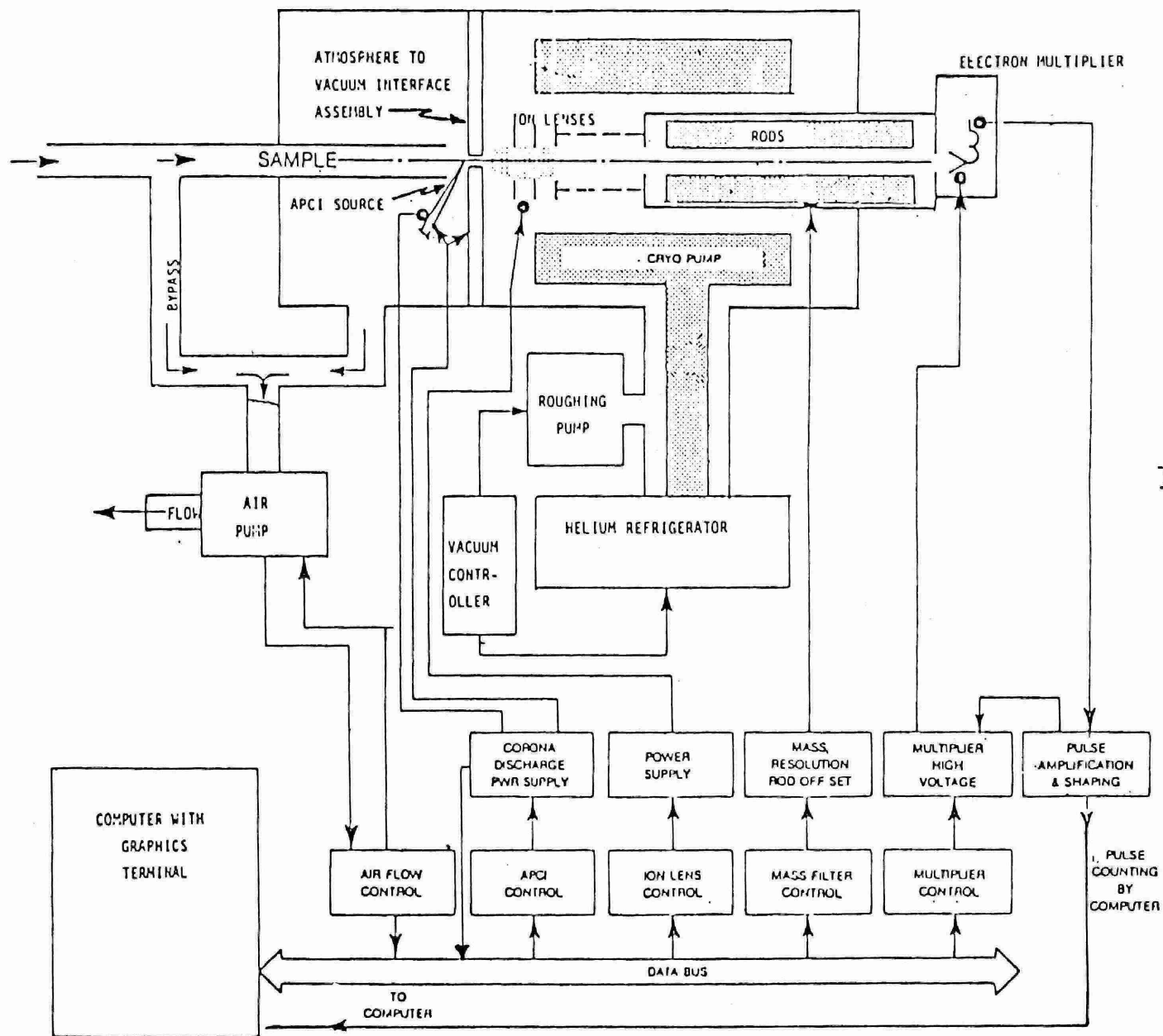
Figure 3.4 Positive ion spectrum obtained with a PCB coated tube inserted in the sampling line.

output devices. The computer system exercises control over the remainder of the TAGA<sup>TM</sup> system through a digital control interface.

In the direct ambient air sampling mode, a high capacity air pump draws ambient air through a inlet duct, typically 22 mm O.D., 19 mm I.D. borosilicate glass tubing, in the air sampling network at variable flow rates, 0.5 to 9 litres per second. Large flow rates ensure minimum sample memory effects on the duct walls. A small portion (typically 1-2 l/s) of the input gas flows through the APCI region, and the rest of the flow is by passed. Reactant ions are generated in the corona discharge region form the sample gas, and react with molecules of the trace as they cross the reaction zone to the flange containing the vacuum orifice. Electric fields are applied in the APCI source to lead the signal ions through the fine aperture of the atmosphere - vacuum interface and ultimately to the electron multiplier ion detector. The atmosphere -vacuum interface prevents the fine orifice from being clogged with atmospheric particulates, especially under dusty conditions or other adverse situations, e.g., direct stack gas monitoring. This interface also reduces any signal loss or unwanted mass spectral alteration due to clustering or condensation effects around the ions, especially arising from the expansion of the ion-air mixture into vaccum.

The high speed cryogenic pumping system removes the neutral molecules from the incoming beam, while the ions are focused into the entrance of the quadrupole mass filter for analysis according to their mass-to-charge ratio ( $m/z$ ).





SIMPLIFIED  
TAGA 3000 SYSTEM

Figure 3.5

From a completely shutdown condition the vacuum system takes approximately 4.0 hours to reach its operational condition. The cryopump can accept gas deposition for 30-50 hours of continuous sampling before the necessity of recycling, which is automatically accomplished either overnight (10 hr.) or over a weekend (60 hr.)

The 15.88 mm diameter precision quadrupole with high efficiency ion insertion system provides a mass range normally to 560 atomic mass unit (amu), with better than unit resolution if desired. Computer control is the standard mode of operation; however, manual override, or hybrid AUTO-MANUAL, are also available for specific purposes.

The signal handling system receives pulses from the electron multiplier, transmitting them on to the computer, if in AUTO MODE, or providing analog outputs, if in MANUAL MODE.

### 3.1.6 Optimization of the MOE TAGA<sup>TM</sup>3000 system for the Real Time Detection of PCBs.

#### 3.1.6.1 General System Check-out and optimization.

Prior to any attempt to optimize the MOE TAGA<sup>TM</sup>3000 system for the real-time detection of PCBs, the instrumentation should be subjected to a thorough system check-out by a qualified service personnel. This procedure is very important, especially when the system has undergone any service involving the vacuum, electronic, ion optics and/or data handling system. After the satisfactory completion of this total system check-out, a system optimization is carried out to obtain maximum information from the TAGA<sup>TM</sup>3000 ion signal.

These system check-out and optimization procedures are described in the TAGA<sup>TM</sup>3000 Operator's Manual (Ref. 8). Figure 3.6 illustrates an example of the fine tuning of lens 1 (one) by comparing the number of ions per second at  $m/z = 18.8$  for  $H_3O^+$  at various L1 voltages, e.g. 60V, 58V, 56V, 54V, 52V, etc. Regular optimization is carried out once in every 3-4 months. This involves the optimization of interface curtain gas flow, discharge current (DI), interface plate voltage (IN), ion lenses (F1, L2, L3, L4 and L5), rod off-set (RO), resolution (RE), multiplier voltage (MU) and mass calibration (M). It is also important to maintain the sampling duct and plenum chamber clean. The corona discharge needle should be inspected regularly, and should be replaced if excessive wear is observed. The pressure and temperature of the cryogenic pump region should be inspected frequently so that any orifice clogging can be detected immediately. Any rapid or gradual orifice clogging will result in loss in sensitivity and inaccurate quantitation.

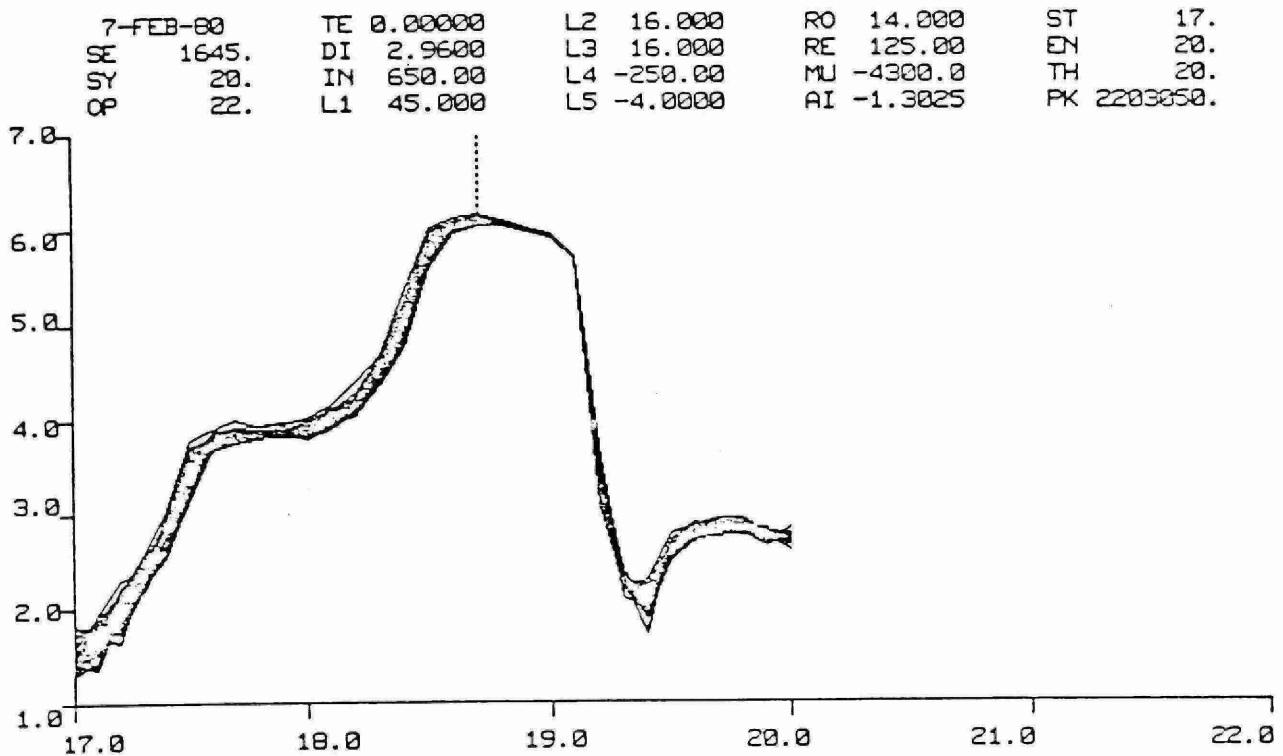
#### 3.1.6.2 Preparation of Constant PCB Source.

In order to optimize the MOE TAGA<sup>TM</sup>3000 system for the real-time detection of PCBs, a constant source of PCB vapor is necessary. This can be achieved by passing prepurified air through a stainless steel tube coated with a commercial PCB mixture at constant temperature.

##### Material

- Commercial PCBs such as Aroclor 1221, 1248, 1254 and 1260 obtained from the Ministry.
- Acetone, pesticide grade, purchased from Fisher Scientific Co. Ltd., Toronto, Ontario.

Figure 3.6 FINE TUNING OF LENS 1



TAG3B7RT  
MARKER, RATE?18.8

18.8 1325400.  
18.8 1309200.  
18.8 1301400.  
18.8 1305600.

PARAMETER?L1 60

18.8 522600.  
18.8 536400.  
18.8 519000.  
18.8 504000.

PARAMETER?L1 58

18.8 840600.  
18.8 864600.  
18.8 832200.  
18.8 867600.  
18.8 858000.

PARAMETER?L1 56

18.8 1191600.  
18.8 1195200.  
18.8 1197600.  
18.8 1199400.  
18.8 1186200.

PARAMETER?L1 54

18.8 1379400.  
18.8 1384200.  
18.8 1355400.  
18.8 1362600.  
18.8 1389000.  
18.8 1378200.

PARAMETER?L1 52

18.8 1396800.  
18.8 1344600.  
18.8 1350000.  
18.8 1357200.  
18.8 1369800.

- Type 304 stainless steel tubing (1/8" or 3.175 mm O.D., 0.020" or 0.5 mm wall thickness) purchased from Chromatographic Specialities Limited, Brockville, Ontario.
- 1/8" (3.175 mm) Swagelok unions and plugs purchased from Avon Valve and Fitting, Scarborough, Ontario.
- Polypropylene wide mouth jar with screw closure (No. B7570-16) purchased from CANLAB, Toronto, Ontario.

#### Appartus

- Hamilton microsyringe (250-1,000 ug) capacity to inject an Aroclor solution into the stainless steel tube, available from Chromatographic Sepcialties Limited, Brockville, Ontario.
- Chemical balance, readable to 0.001 g.
- Weighing boat, spatula, glass rod, funnel, volumetric flask, beaker, label and other small items necessary to prepare solutions.
- Fumehood, organic waste bottle, sink, oven and other standard laboratory supplies to handle toxic chemicals.
- 7/16" (11.1 mm) and 1/2" (12.7 mm) open end wrenches to tighten Swagelok fittings.
- Charcoal filter (1.8 kg activated charcoal, 6-14 mesh) to

absorb PCBs, available from Fisher Scientific Co., Toronto (No. 5-685B).

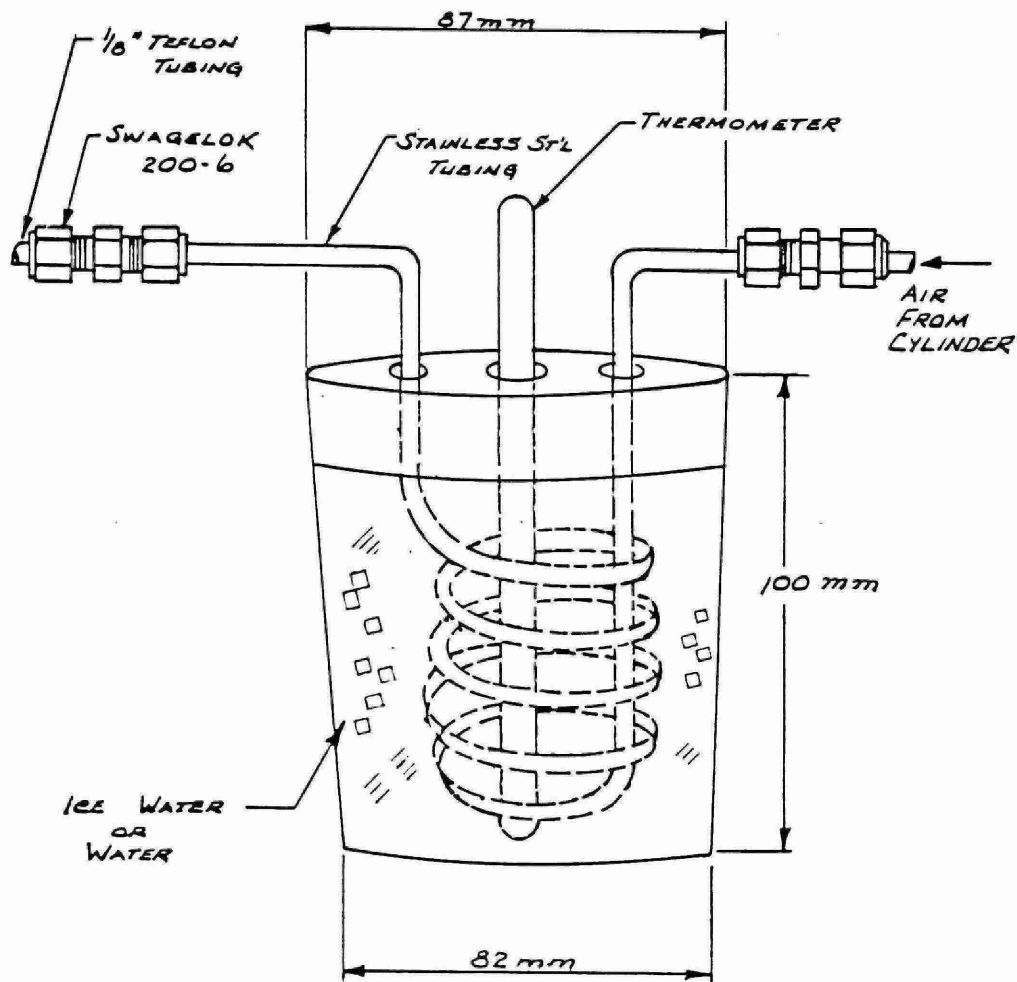
- 1/8" (3.17 mm) O.D. polyethylene or nylon tubing available from Chromatographic Specialties Ltd., Brockville, Ontario.
- Cylinder of prepurified air, pressure gauge, valves and tubing to produce a gentle stream of air.

#### Preparation

Wear disposal gloves, goggles and a labroatory coat, and organize the fumehood and the working area to minimize possible contamination, before the following steps.

Prepare a solution of Aroclor 1248 (or other Aroclors) in acetone in the concentration range 0.05 - 0.2 g/ml. Cut a piece of the 304 stainless steel tubing, 50-60 cm long, and clean the piece with acetone. Air dry the tube in a fumehood.

Hold the tube at a slant position over a waste beaker, gently add the Aroclor solution using a misrosyringe, while rotating the tube to enable even coating of the innner wall. After adding 0.5 -1.0 ml of the solution, the tube is left standing in the waste beaker to dry the solvent. Then, the tube is coiled (4-6 cm diameter) as shown in Figure 3.7. The ends of the tube are passed through the plastic cap and appropriate Swagelok fittings are connected. Then, a tubing is attached to



PCB CONSTANT SOURCE

FIGURE 3.7

the exit end to lead the vapor to a charcoal trap. Prepurified air is gently added to the entrance of the PCB coated tube to evaporate any remaining acetone, because acetone interferes with benzene chemical ionization. After this thorough drying, both ends are capped and the source is labeled accordingly. The temperature of this PCB source can be adjusted by adding ice-water or warm water and measured with a thermometer. If accurate control of the temperature is necessary, this can be achieved by circulating water from a constant temperature bath. Approximate compositions of these Aroclor products are shown in Table 3.1 (Ref. 1). Aroclor 1221 can be used to optimize the TAGA<sup>TM</sup>3000 until for mono- and bi-chlorobiphenyls, whereas Aroclor 1248 is suited for tri- and tetrachlorobiphenyls, and Aroclor 1260 for the penta- and hexa species.

**Table 3.1**

Chlorobiphenyl Composition	Molecular Composition of Some Aroclors				
	1221	1242	1248	1254	1260
C <sub>12</sub> H <sub>10</sub>	11	0.1	-	0.1	-
C <sub>12</sub> H <sub>9</sub> Cl	51	1	-	0.1	-
C <sub>12</sub> H <sub>8</sub> Cl <sub>2</sub>	32	16	2	0.5	-
C <sub>12</sub> H <sub>7</sub> Cl <sub>3</sub>	4	49	18	1	-
C <sub>12</sub> H <sub>6</sub> Cl <sub>4</sub>	2	25	40	21	-
C <sub>12</sub> H <sub>5</sub> Cl <sub>5</sub>	0.5	8	36	48	12
C <sub>12</sub> H <sub>4</sub> Cl <sub>6</sub>	0.01	1	4	23	38



Table 3.1 (continued)

Chlorobiphenyl Composition	Molecular Composition of Some Aroclors				
	1221	1242	1248	1254	1260
C <sub>12</sub> H <sub>3</sub> Cl <sub>7</sub>	0.01	0.1	-	6	41
C <sub>12</sub> H <sub>2</sub> Cl <sub>8</sub>	0.01	-	-	0.01	8
C <sub>12</sub> H <sub>2</sub> Cl <sub>9</sub>	-	-	-	-	-
C <sub>12</sub> Cl <sub>10</sub>	-	-	-	-	-

Source: O . Hutzinger, S. Safe and V. Zitko:  
The Chemistry of PCBs, CRC Press, Cleveland, Ohio  
(1974)

### 3.1.6.3 Optimization of MOE TAGA<sup>TM</sup> for Real-Time PCB Detection.

#### 3.1.6.3.1 PCB and Benzene Flow System.

Figure 3.8 is a flow diagram of the carrier, reagent and sample gases for the optimization of the MOE TAGA<sup>TM</sup>3000 for the real-time detection of PCBs. Prepurified air from a cylinder (obtained from Gas Dynamics in Toronto, or Matheson of Canada in Whitby, Ontario) is cleaned by passing it through a molecular sieve purification train. After the purification the air is transported through 1/8" (3.175 mm) O.D., 0.020" (0.508 mm) wall thickness stainless tubing to a manifold where the flow is split into 3 channels. Each channel has a precise needle valve and an accurate 150 mm Matheson flowmeter Series 7600 to regulate the air on the surface of the benzene in the bubbler. The vapor is then carried through a 1/8" (3.175 mm) O.D. Teflon tube into a 22 mm Pyrex glass tube attached to the TAGA<sup>TM</sup> plenum chamber. The second channel, shown in the middle of Figure 3.8, supplies constant PCB vapor to the plenum chamber by passing the air through the constant PCB vapor source prepared in the last section.

Please note that the PCB vapor is transported through a straight stainless steel tube (3.175 mm O.D.), aligned at the centre of the Pyrex tube to approximately 1 cm from the tapered open end in order to obtain best PCB transport into the ionization region.

The third channel adds the clean air to maintain suitable gas dynamics; that is, stable and memory-free response. Table 3.3 shows typical flow rates used to optimize the TAGA<sup>TM</sup>3000 unit for the real-time detection of PCBs.

Table 3.3 Typical Flow Rates for Real-Time PCB Detection

Interface Curtain Gas (N <sub>2</sub> ):	1.0 l/min.
Benzene Bubbler (Tube 610):	3.0 ml/min.
Carrier Air (Tube 604):	4.2 l/min.
Constant PCB Source* (Tube 600):	85 ml/min.

\*The flow rate varies by the temperature and type of the constant PCB vapor source, since monochlorobiphenyls and dichlorobiphenyls are much more volatile than hexachlorobiphenyls. The optimum flow rate must be experimentally decided upon by the TAGA<sup>TM</sup>3000 operator.

#### 3.1.6.3.2 Optimization of Benzene Reactant Ion.

Using the flow rates described in Table 3.3, but with the constant PCB source valve remaining closed, the MOE TAGA<sup>TM</sup>3000 system is optimized for the benzene signal. In the positive mode fast mass scans are generally repeated within a very narrow mass range, say,  $m/z = 76$  to  $m/z = 80$  (Enter ST = 76, EN = 80 and then RT in response to the TAGA? prompt).

FIGURE 3.8 FLOW DIAGRAM OPTIMIZATION FOR REAL-TIME PCB ANALYSIS

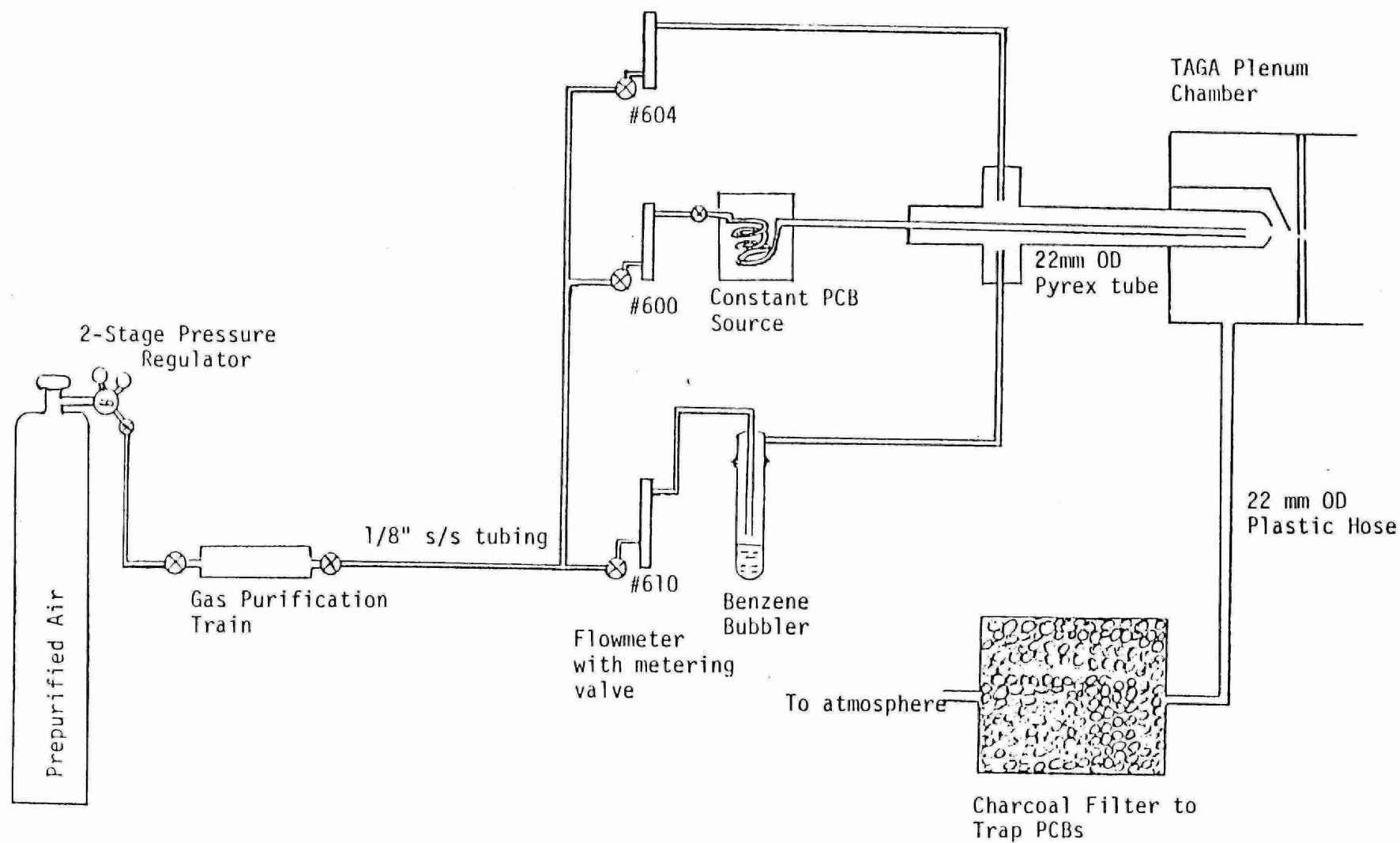


TABLE 3.2 Ion Lens Optimization for Real-Time Detection of Dichlorobiphenyl

PARAMETER 7L1 43	PARAMETER 7L2 16	PARAMETER 7L3 14
221.9 3620.	221.9 3235.	221.9 5740.
221.9 3328.	221.9 3405.	221.9 7449.
221.9 2821.	221.9 3594.	221.9 4860.
221.9 3401.		221.9 5973.
		221.9 5916.
PARAMETER 7L1 45	PARAMETER 7L2 18	PARAMETER 7L3 16
221.9 2731.	221.9 5759.	221.9 4920.
221.9 3295.	221.9 4951.	221.9 6508.
221.9 3230.	221.9 5115.	221.9 5830.
221.9 3563.	221.9 4466.	221.9 6141.
	221.9 5096.	221.9 5638.
		221.9 7578.
PARAMETER 7L1 47	PARAMETER 7L2 20	PARAMETER 7L3 18
221.9 3562.	221.9 6046.	221.9 5357.
221.9 3053.	221.9 5713.	221.9 6280.
221.9 3121.	221.9 4423.	221.9 5479.
221.9 3116.	221.9 5135.	221.9 5159.
	221.9 6597.	221.9 6755.
PARAMETER 7L1 49	PARAMETER 7L1 22	
221.9 3745.	221.9 247.	
221.9 2595.	3	
221.9 2988.	PARAMETER 7L1 43	PARAMETER 7L3 20
221.9 3657.	PARAMETER 7L2 22	221.9 4523.
PARAMETER 7L1 51	221.9 6021.	221.9 5922.
221.9 3511.	221.9 4665.	221.9 4870.
221.9 2821.	221.9 5577.	221.9 3823.
221.9 2686.	221.9 4308.	221.9 5479.
221.9 3208.	103 67 109	221.9 5485.
221.9 2617.	PARAMETER 7L2 24	
PARAMETER 7L1 43	221.9 4173.	
221.9 3770.	221.9 4369.	
221.9 3590.	221.9 3314.	
221.9 3764.		

221.9 6999.  
103 67 109

PARAMETER 7L4 -230

221.9 5192.  
221.9 6934.  
221.9 5021.  
221.9 5887.  
221.9 6894.  
221.9 5367.

03 127 109

PARAMETER 7L4 -240

221.9 5978.  
221.9 7237.  
221.9 7060.  
221.9 7938.  
221.9 6708.

12

PARAMETER 7L4 -250

221.9 7002.  
221.9 5957.  
221.9 6721.  
221.9 6367.  
221.9 5974.

09

PARAMETER?

The computer display can be either in a logarithmic format by commanding Format Control FO = 4 as shown in Figure 3.9, or in a linear format using FO = 17, as shown in Figure 3.10. The TAGA and DATA parameters are listed in Table 3.4.

The log format is convenient for rough tuning for its wide dynamic range, whereas the linear format is suited to fine tuning the instrument. Various TAGA parameters (DI, IN, L1, L2, L3, L4, L5, MU, PK, RO) may be adjusted to obtain the best peak shape and strength by a fashion similar to the one described in Section 3.1.6.1.

After the optimization of the ion optics, the benzene bubbler and carrier gas flow rates can be adjusted to give the best signal; typically, 1.5 million to 2.5 million ion counts per second.

#### 3.1.6.3.3 Optimization of MOE TAGA for Real-Time PCB Detection.

After the completion of benzene ion optimization described in the last section, the clean air is now passed through the constant

FIGURE 3.9 Benzene Ion Optimization (Log Intensity Display)

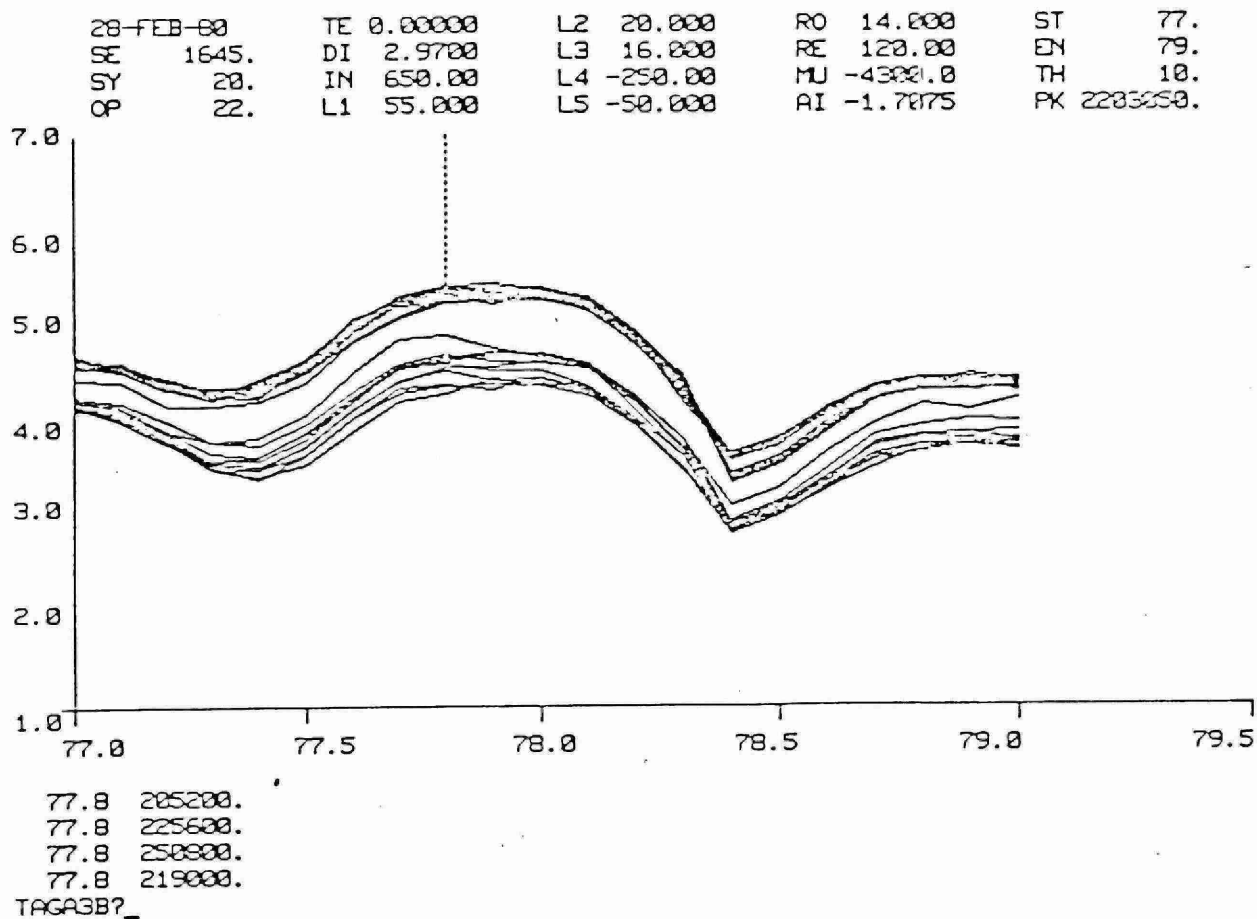


FIGURE 3.10 Benzene Ion Optimization (Linear Intensity Display)

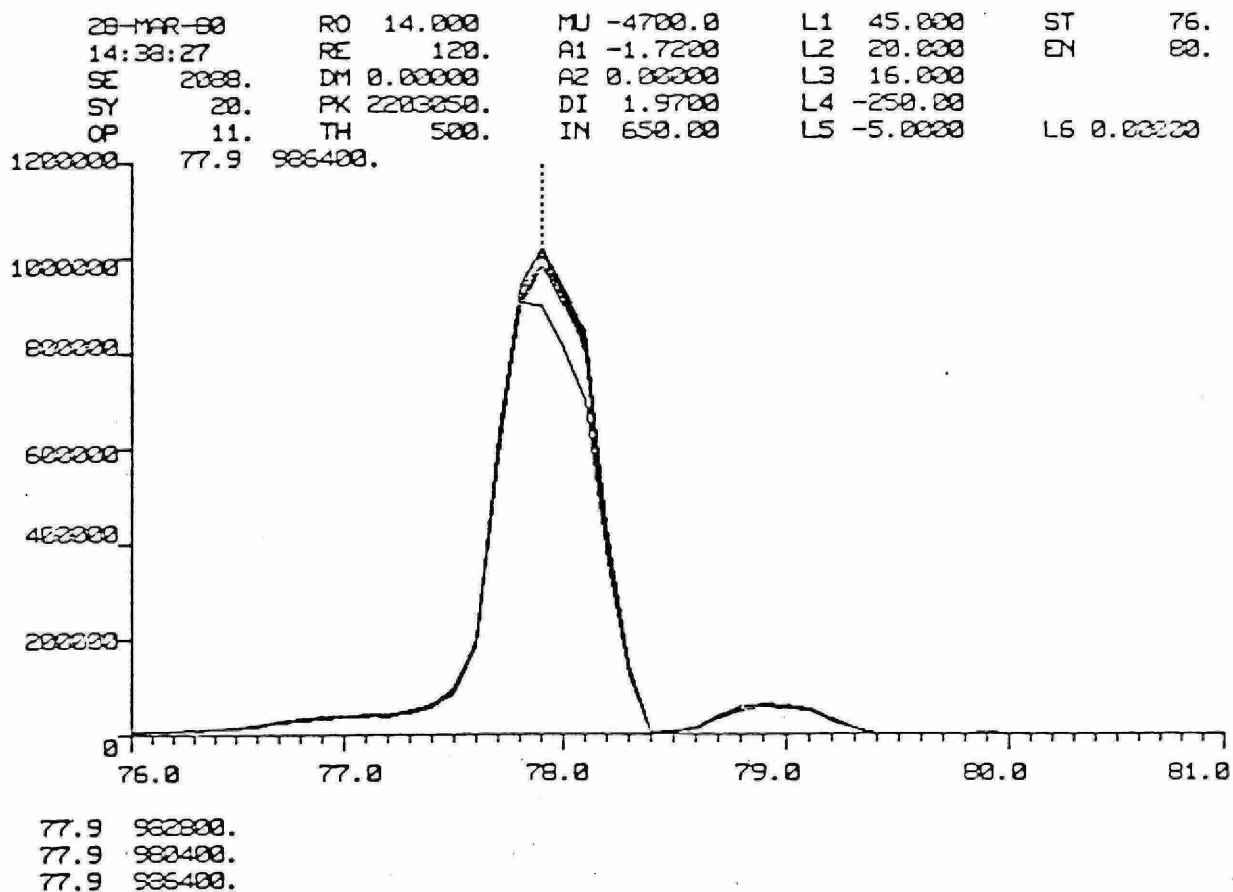
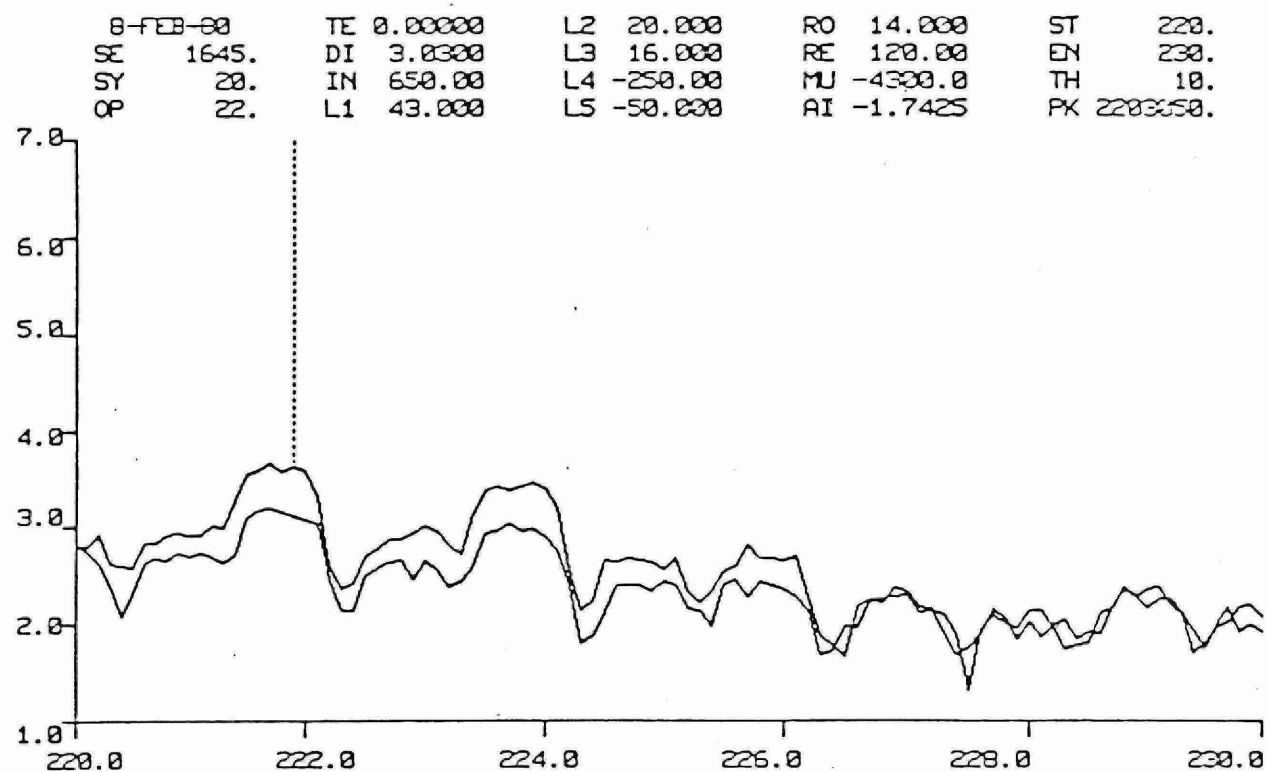


Figure 3.11 ION LENS OPTIMIZATION FOR REAL-TIME DETECTION OF DI-  
CHLOROBIPHENYL - L5



PARAMETER 7.5 -5	PARAMETER 7.5 -30
221.9 5774.	221.9 6997.
221.9 6109.	221.9 5730.
221.9 7065.	221.9 4983.
221.9 7815.	221.9 5820.
221.9 7158.	221.9 4463.

PARAMETER 7.5 -10
221.9 7358.
221.9 6112.
221.9 6546.
221.9 5406.
221.9 8890.

PARAMETER 7.5 -15
221.9 6987.
221.9 6047.
221.9 6492.
221.9 6244.
221.9 5702.

PARAMETER 7.5 -20
221.9 5635.
221.9 6003.
221.9 6775.
221.9 7615.
221.9 5742.

PARAMETER 7.5 -25
221.9 6510.
221.9 6682.
221.9 6694.
221.9 6383.
221.9 6228.



Table 3.4

TAGA and DATA Parameters

TAGA version B01	
TAGA PARAMETERS	
*A1 Air flow (bypass)	
*A2 Air flow (APCI)	
BO Bottom of linear intensity	
DI Discharge current	
EN end mass for mass scan	
FO Format control	
IN Interface plant voltage	
L1 Lens 1 voltage	
L2 Lens 2 voltage	
L3 Lens 3 voltage	
L4 Lens 4 voltage	
L5 Lens 5 voltage	
L6 Lens 6 voltage	
MU Multiplier voltage	
M1 Mass 1 for MI & Monitor mass	
M2 Mass 2 for MI	
M3 Mass 3 for MI	
M4 Mass 4 for MI	
M5 Mass 5 for MI	
M6 Mass 6 for MI	
M7 Mass 7 for MI	
M8 Mass 8 for MI	
OP Operator number	
PE Period between meas. (sec.)	
PK Peak measurement control	
RE Resolution of mass filter	
RO Rod offset voltage	
*SE Sequence number	
ST Start mass for scan	
*SY System serial number	
TH Threshold for intensity	
TO Top of linear intensity	
TT Termination time (min.)	
*Values set by program	
TAGA FUNCTIONS	
CA Calibrate mass	
EX Exit to system monitor	
LP Load parameters from a file	
MI Multiple ion data to file	
PA Parameter print	
PO Polarity reversal	
RM Real time multiple ion	
RT Real time spectra	
SC Scan spectra data file	
SI Single ion	
SP Save parameters to a file	
TI Title entry	
PEAK & INTENSITY STATISTICS	
PK=ABCCDDD where	
A=difference interval (norm.	
B=window width (+/-(B+1)/10	
CC=maximum meas. time (CC/15)	
DDD=ion sjper sample (DDD*10 IONS)	
When A=0, window is zero width	
AB=00 smaple at mass-0.2 AMU	
AB=01 sample at mass-0.1 AMU	
AB=02 sample at mass+0.0 AMU	
AB=03 sample at mass+0.1 AMU	
AB=04 sample at mass+0.2 AMU	
DATA version B01	
DATA PARAMETERS	
BO Bottom of linear intensity	
EN End of mass or sequence no.	
FO Format control	
MA Mass for single ion plot	
ST Start of mass or sequence no.	
TO Top of linear intensity	
DATA FUNCTIONS	
CR=1,2 Clear register	
EX Exit to system monitor	
FR=1,2 Associate file with reg.	
LR=1,2 Load register with scans	
PA=1,2 Parameter print for reg.	
PC=1,2 Plot ratio of registers	
PD=1,2 Plot difference of reg.	
PR=1,2 Plot register contents	
SI=1,2 Single ion (MA) plot	
TR=1,2 Tabulate reg. contents	
FORMAT CONTROL FOR TAGA OR DATA	
FO=0 gives none of features below	
FO=sum, of selected changes below	
1-linear intenisty MI,PR,RT,SC,SI	
2-bar graph in MI, RT, SC	
4-no erase at right margin in	
8-no graphics in MI, SC	
16-fine horizontal scale in DATA	

PCB vapour source to introduce PCB vapor into the plenum chamber. With a constant amount of the PCB vapor flowing into the plenum chamber, the mass spectrometer scans repetitively within a narrow mass range, say, 10 amu about each PCB species, that is

Mass range 1	$m/z = 186 - 196$ for monochlorobiphenyl
Mass range 2	$m/z = 220 - 230$ for dichlorobiphenyl
Mass range 3	$m/z = 254 - 264$ for trichlorobiphenyl
Mass range 4	$m/z = 288 - 298$ for tetrachlorobiphenyl
Mass range 5	$m/z = 320 - 330$ for pentachlorobiphenyl
Mass range 6	$m/z = 356 - 366$ for hexachlorobiphenyl

As an example, choose an Aroclor 1221 constant PCB vapor source to optimize the TAGA<sup>TM</sup>3000 system in mass ranges 1 and 2. Figure 3.11 shows the optimization of Lens 5 by varying the voltage at 5 volt intervals, and leaving the other parameters constant, i.e., DI, IN, L1, L2, L3, L4, RO, RE, MU, ST, EN, TH and PK. Table 3.2 lists responses in ions per second at  $m/z = 221.9$ , when L1, L2, L3 or L4 are independently varied. Similarly, DI, IN, RO, RE, MU can be changed to obtain the best peak shape and strength. After the initial optimization has been completed in the log display mode, the intensity display may be switched to the linear mode. Fine tuning can be accomplished by slightly changing these ion optics parameters. The best parameters obtained in this fashion, will then be typed into a parameter table in the PCBMON program, which has been specially developed for the PCB analysis by integration.

### 3.2 PCB Wire Integrator.

During the previous development described in Ref. 6 it was found

that the detection limits for monochlorobipheny to pentachlorobiphenyl on a real-time basis are in the range of 20 - 50 ng/m<sup>3</sup>. These detection limits are far too high to determine atmospheric PCB contents, and it is necessary to improve these detection limits.

An approach to solve this problem is to precollect PCBs in air for a period of time before analysis. SCIEX INC had developed, in co-operation with the National Research Council of Canada, a collection or sample integration system, consisting of a glass tube 10 cm x 6 mm O.D. containing a 3 cm length of platinum mesh coated with silivone oil (Ref. 9, p. 3). This idea has been expanded to the use of a conical coil of 0.813 mm diameter chromel-A wire coated with a thin layer of a gas-liquid-chromatographic (GLC) liquid phase (Ref. 6). This system is designed to combine the following features:

- (a) No extensive sample handling and/or conditioning is necessary between sample collection and analysis, that is, this system does not require an air bag, cold storage, wet chemical sample clean-up, syringe injection or other techniques practiced in common environmental laboratories.
- (b) Rapid transfer from sampling position to analysis position, to minimize turn-around time for sampling.
- (c) Compatible with sampling periods from one to several minutes.
- (d) Can easily fit the TAGA<sup>TM</sup>3000 ambient air sampling front end.
- (e) Can be calibrated directly with a known PCB vapor source.

- (f) Has a potential for automated operation in the future.
- (g) Capable of separating chemicals of interest from moist stack gas, or from wet ambient air, i.e., capable of ambient air and flue gas analysis.

### 3.2.1 Construction of Wire Integrator.

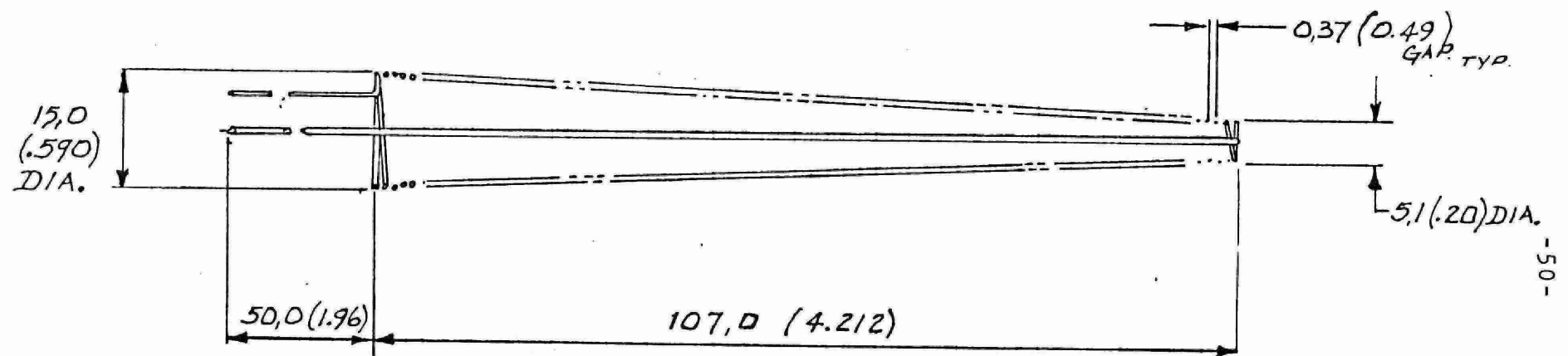
Figure 3.12 indicates a machining diagram of the PCB adsorber coil made of chromel-A wire. This coil is available from SCIEX stock (TS01452), and should be free from any sharp bend or coils touching each other. Coils should be cleaned with hexane, acetone and methanol to remove any impurities before coating with silicone oil.

An attempt was made to improve adsorption efficiencies by etching the surface of this coil with a mineral acid such as hydrochloric acid or sulfuric acid. However, the etched coil coated with silicone oil produced a very broad desorption peak, perhaps due to the extreme activation of the surface. It did not improve the adsorption/desorption characteristics and therefore no further work has been carried out.

### 3.2.2 Coating of PCB Adsorber Coil.

The following GLC liquid phases were purchased from Chromatographic Specialties Limited, Brockville, Ontario.

- OV-101 (100% methyl silicone)
- OV-7 (20% phenyl - 80% methyl silicone)
- OV-17 (50% phenyl - 50% methyl silicone)
- SP-2250 (50% phenyl - 50% methyl silicone)
- Dexsil 400 (carborane-phenyl silicone)



# PCB ADSORBER COIL

Figure 3.12

MATERIAL: 0.032" (0.813 mm) DIA.  
CHROMEL-A WIRE

Typically, a 5-6% solution is prepared by weighing a GLC phase and dissolving it in acetone. Any solution containing less than 5% has been found to be too diluted to form a stable film. On the other hand, a more concentrated solution, say 8-12%, tends to give very thick and viscous films, often resulting in the broadening of the desorption peak to be discussed later.

The coating of the adsorption coil is made by placing a clean coil in the solution in a tall beaker or cylinder for a few minutes, then air drying in a large beaker placed in a fumehood. Make sure that the film is applied evenly, by gently rotating and tilting the coil, while the solvent is evaporating. After air-drying the coil, it is conditioned overnight at 150° C in an oven. The finished coil is usually placed in a jar and labelled for storage at room temperature. Each coil, when properly prepared and operated, lasts for a few months of continuous use.

A brief study has been made to compare adsorption efficiencies of tetrachlorobiphenyls by different GLC liquid phases. Responses relative to that of a 1:3 mixture of OV-17 and SP-2250 are shown in Table 3.5. However, these values should be interpreted with caution, because they were obtained at only one m/z using only one coil each per GLC liquid phase. It is possible that the adsorption efficiencies of these materials depend on sample gas temperature, PCB species, shape of the coil and many other parameters.

For the PCB analysis of ambient air and stack gas, coils coated with either OV-7 or OV-17 were used. Because the total analytical system was calibrated each day of work using the same coil under the same conditions, the accurate adsorption efficiency is not of our prime concern as long as the coil can reproduce results for a reasonable length of time.

Table 3.5

Comparison of PCB Adsorption Efficiencies  
by Several GLC Liquid Phases

<u>GLC Phase</u>	<u>Relative Response (5) at m/z = 292</u>
OV-17	89.7
SP 2250	96.6
OV-17 + SP2250(1:3)	100.0
OV-101	54.2
OV-7	74.0
Dexsil 400	35.9
Uncoated	10.8

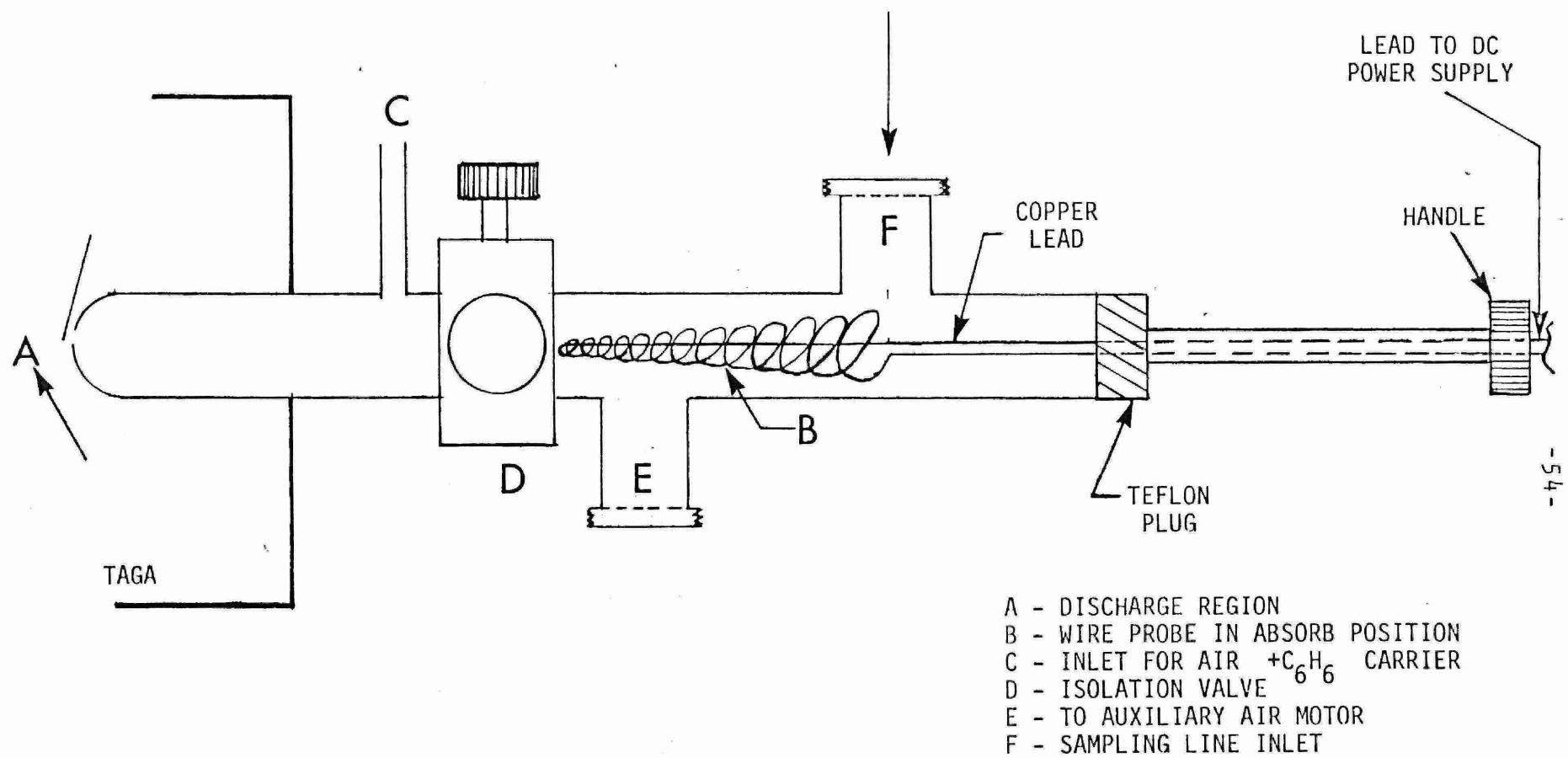
### 3.2.3. PCB Wire Integrator System.

Figure 3.3 is a flow diagram of the PCB wire integrator inlet system. During the sampling period the plenum region is isolated from the inlet line by a closed nylon stopcock valve, and a flow of pure carrier, prepurified air, containing benzene vapor is maintained past the needle. An air pump draws ambient air or sample gas at 1.5-2.5 l/s past the integrator for the desired sampling time (typically 2 minutes), after which the valve is opened and the probe moved forward into the desorb position in the plenum chamber. At this point the Teflon plug, holding a pair of copper rods to support the coil, maintains the isolation of the discharge region from the inlet line. The collected sample is desorbed from the wire by heating it resistively with a ca. 12v D.C. pulse of 55 second duration. The signal is monitored by multiple selected ion monitoring at selected masses of interest. When the desorption is finished, the current is turned off and the wire probe is returned to the sampling position to begin another cycle. The response is fed into the PDP-11 computer. This is further discussed in Chapter 4.

The integrator is designed to sample from a gas containing a concentration  $C_1$  of PCB, drawn past the probe at a flow rate  $F$ , and to transfer the collected sample into a carrier gas at a lower flow rate  $F_2$ , producing a concentration  $C_2$  in the carrier. If the collection time is  $t_1$  and the collection efficiency of the probe is  $K$ , then the amount collected on the coils will be  $K C_1 F_1 t_1$ . When this amount is desorbed into the carrier in a time  $t_2$ , a concentration  $C_2 = K C_1 F_1 t_1 / F_2 t_2$  is produced.

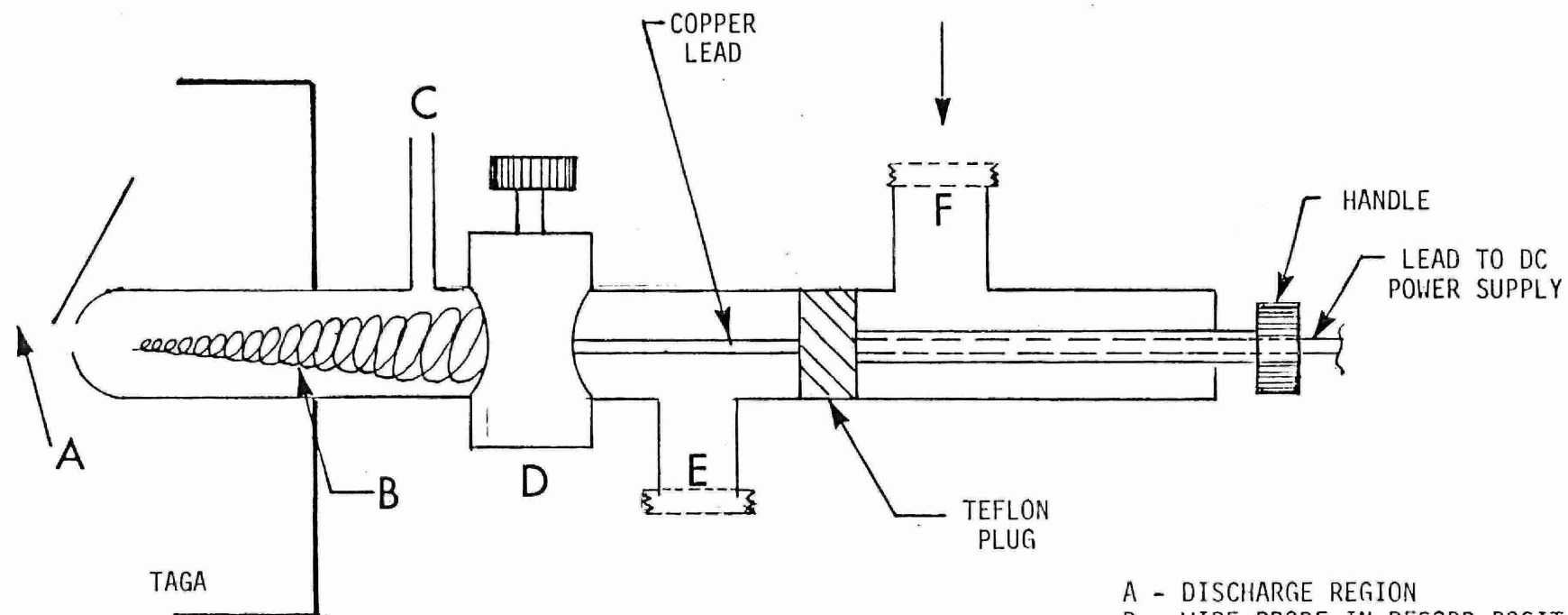
Since the response of the system is proportional to the





WIRE INTEGRATOR INLET SYSTEM  
 ABSORB POSITION

Figure 3.13(a)



- A - DISCHARGE REGION
- B - WIRE PROBE IN DESORB POSITION
- C - INLET FOR AIR +  $C_6H_6$  CARRIER
- D - ISOLATION VALVE
- E - TO AUXILIARY AIR MOTOR
- F - SAMPLING LINE INLET

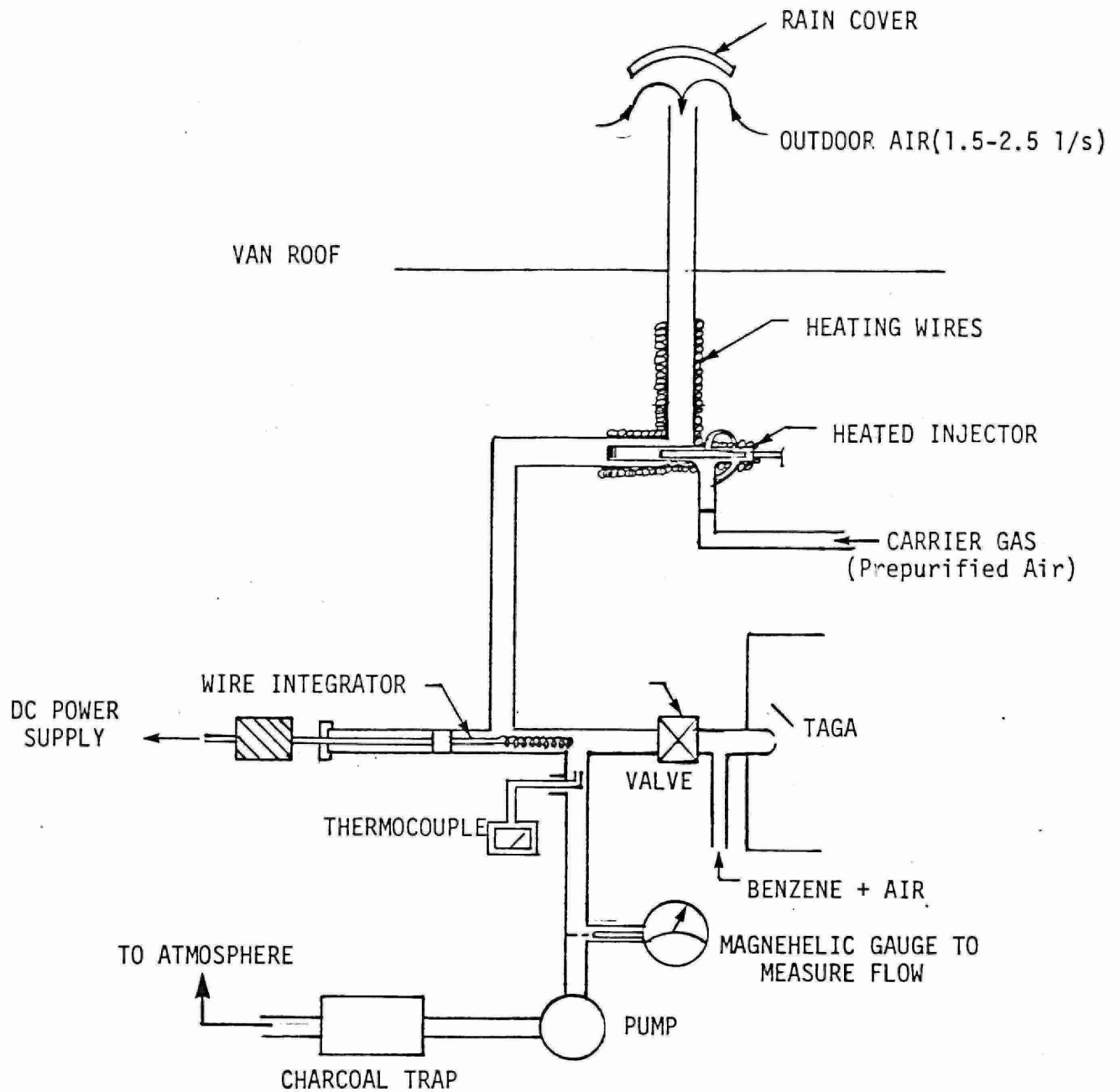
WIRE INTEGRATOR INLET SYSTEM  
DESORB POSITION

Figure 3.13b

concentration of the trace gas in the reaction region, the total enhancement over the real-time sampling is given by  $C_2/C_1 = KF_1t_1/F_2t_2$ . The measured enhancement range will be discussed later.

#### 3.2.4. Ambient PCB Measurement and Calibration by Integration.

Figure 3.14 is a flow diagram of the total sampling system for the measurement of PCBs in ambient air and for the calibration of the system using a calibration mixture. Figure 3.15 is a photo of the interior of the MOE TAGA van, when ambient air is analyzed for PCBs. Ambient air is drawn through the roof port at 1.7 l/s, and is heated with silicone-insulated heaters wrapped around the sampling line to bring the sample air temperature to 50°C, measured just downstream of the PCB wire integrator is placed at the sample collection position for 2 minutes. When the coil is pulled back from the desorb position, it is still hot due to the residual heat even after the voltage pulse is shut off. The sample air temperature is around 70°C at the beginning, however, it remains steady at 50°C after, say, 30-40 seconds from the start of each sampling cycle. After 2 minutes of the sampling, the wire integrator is pushed into the Desorb position and heat is applied to transfer the trapped PCBs to the ionization region. Figure 3.16 shows photographically the van interior, when the PCB calibration is in progress. Known amounts of PCBs are injected into the sampling flow system through a heated injector, which accepts an iso-octane solution containing known amounts of PCBs at a pre-determined rate by the use of a motorized syringe drive. A detailed drawing of the heated injector is shown in Figure 3.17. Prepurified air or nitrogen is supplied at 40-60 ml/s from a compressed gas cylinder through the 600 flowmeter shown in Figure 3.8; that is, the constant PCB vapor source in the Figure is now replaced with this heated injector.



FLOW DIAGRAM OF SAMPLING SYSTEM

Figure 3.14

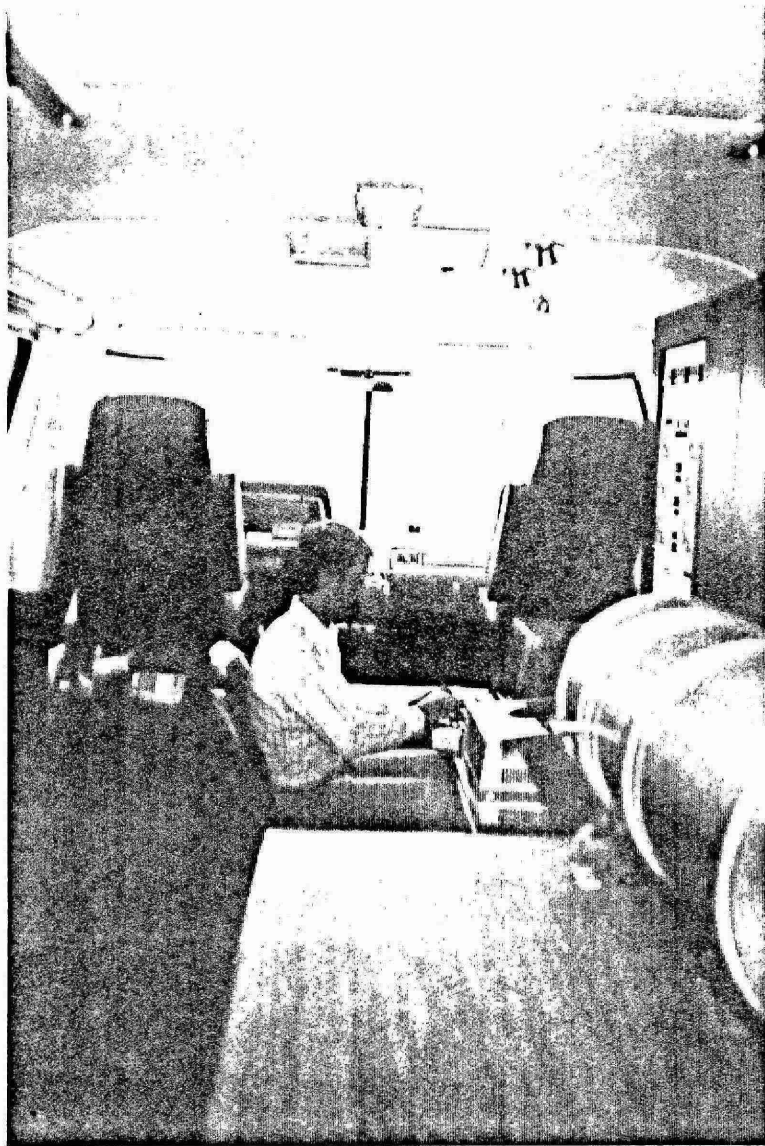


Figure 3.15

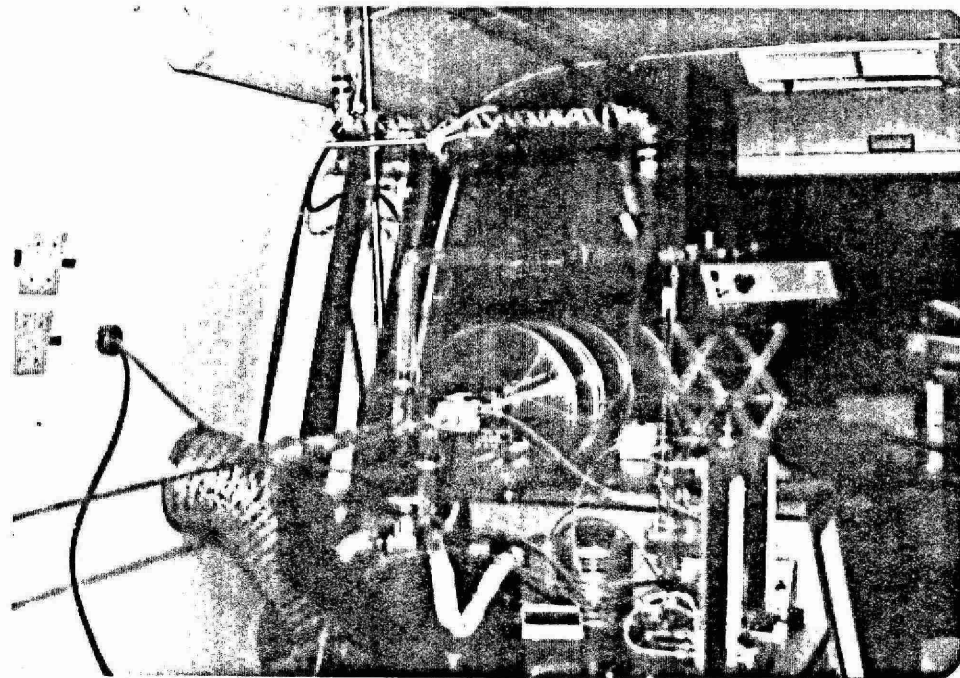
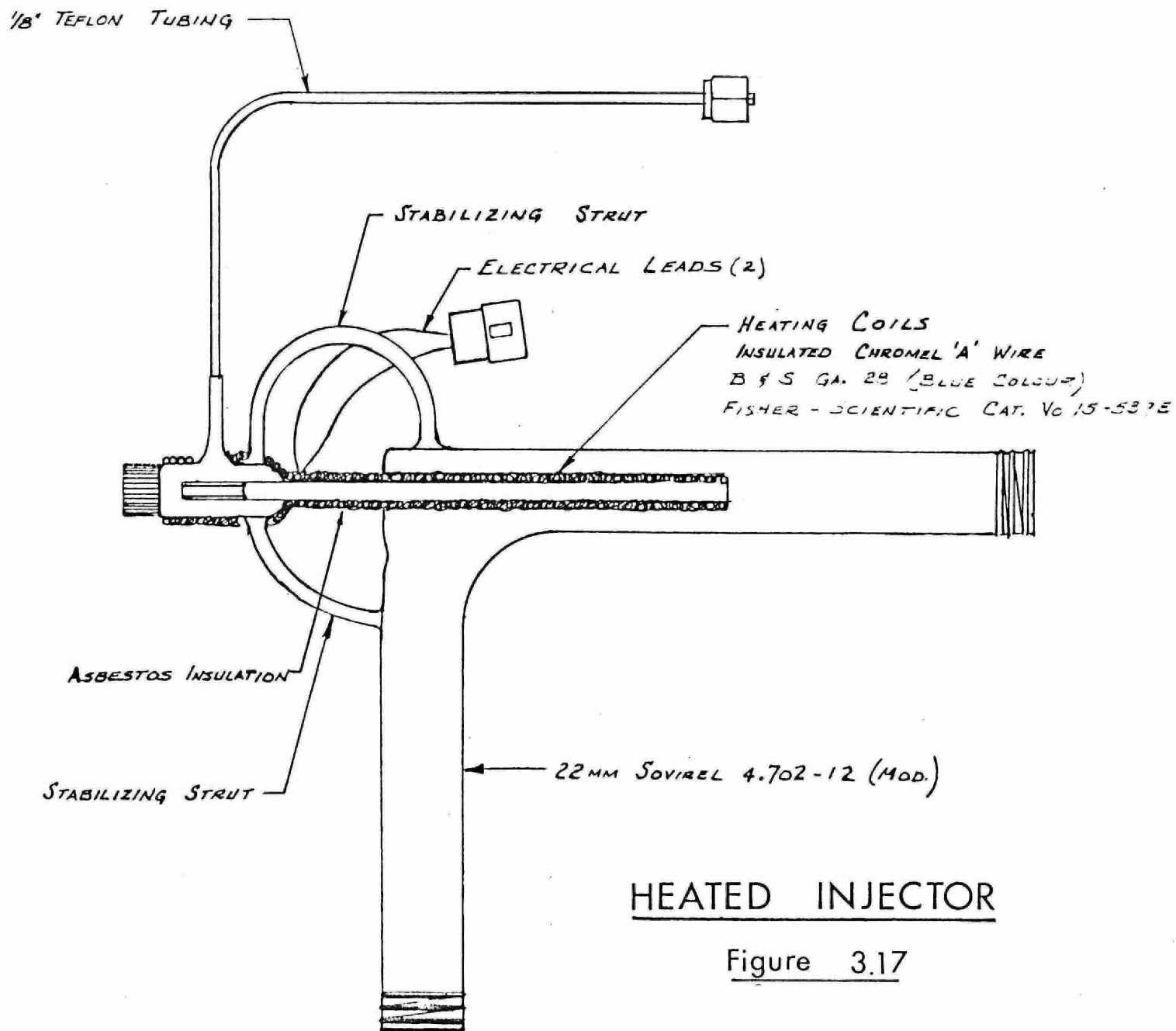


Figure 3.16

Figure 3.15 Photo of Ambient PCB Analysis

Figure 3.16 Photo of PCB Calibration



The temperature of the carrier gas can be measured by inserting a fine thermocouple probe through the septum, with 40-60 ml/s of the carrier gas flowing, and the tube heater on. The optimum temperature to vaporize the PCBs in the solution has been found to be approximately 350°C. When the outdoor temperature was very cold, extra heating was added with heaters wrapped around the main air flow tube. Experimental details will be discussed later.

### 3.2.5 Calibration Mixtures

#### 3.2.5.1 Stock Solution (Solution # 1)

The following chlorinated biphenyls were weighed during a Sartorius Model 2474 balance (Gottingen, West Germany).

- (a) 4-chlorobiphenyl 4.53 mg
- (b) 4,4' - Dichlorobiphenyl 3.07 mg
- (c) 2',3,4 - Trichlorobiphenyl 4.33 mg
- (d) 2,3,5,5' - Tetrachlorobiphenyl 5.60 mg
- (e) 2,3,4,5,6 - Pentachlorobiphenyl 4.68 mg
- (f) 2,2'4,4',6,6' - Hexachlorobiphenyl 10.51 mg

The above chlorinated biphenyls were dissolved with 2,2,4-trimethylpentane (iso-octane), and transferred to a 100 ml volumetric flask. The flask was filled up to the mark with iso-octane. Each microlitre of this solution will contain

45.3 nanograms of 4 - chlorobiphenyl

30.7 nanograms of 4,4' - dichlorobiphenyl

43.3 nanograms of 2', 3,4 - trichlorobiphenyl  
56.0 nanograms of 2,3,5,5' - tetrachlorobiphenyl  
46.8 nanograms of 2,3,4,5,6 - pentachlorobiphenyl  
105.1 nanograms of 2,2', 4,4', 6,6' - hexachlorobiphenyl

The flask was covered with aluminum foil and stored in a refrigerator to prevent any decomposition.

3.2.5.2 Working Solution (Solution # 2)

One ml of the above stock solution ( #1) was pipetted into a clean 25 ml volumetric flask. The solution was diluted to the volume with iso-octane.

Hexane was also tried, but found to be too volatile to maintain the constant volume. Normal octane was used, but the solution did not produce good responses. It has not been investigated in detail if this behaviour of the n-hexane solution was due to some unseen errors in the preparation of the solution, or due to special ion-molecule chemistry.

Each microlitre (ul) of this working solution contains  
1.81 ng of 4-chlorobiphenyl  
1.23 ng of 4,4' - dichlorobiphenyl  
1.73 ng of 2', 3,4 - trichlorobiphenyl  
2.42 ng of 2,3,5,5' - tetrachlorobiphenyl  
1.87 ng of 2,3,4,5,6 - pentachlorobiphenyl  
4.20 ng of 2,2', 4,4', 6,6' - hexachlorobiphenyl

This solution was suited to the calibration of the TAGA<sup>TM</sup>3000 system for the stack gas analysis.



Equivalent concentrations can be calculated as follows:

$$\frac{\text{Syringe drive rate (ul/sec)} \times \text{concentration (ng/ul)} \times \text{sampling time (sec)}}{\text{air flow (m}^3\text{/sec)} \times \text{sampling time(sec)}} \\ = \text{Equivalent Concentration (ng/m}^3\text{)}$$

Table 3.6 a compilation of equivalent concentrations at various syringe drive rates. The syringe drive, Sage Model 341, Fisher Scientific catalogue number 14-831-40, should be calibrated with the same liquid tight syringe and the same solution as those used for actual measurements.

#### 3.2.5.3 Working Solution (Solution # 3)

This solution was prepared by diluting the above working solution (#2) ten-fold, and is suited for the calibration of the TAGA<sup>TM</sup>3000 system, when heavily contaminated ambient or indoor air has to be analyzed for PCBs. Equivalent concentrations may be calculated by dividing the values in Table 3.6 by a factor of 10.

#### 3.2.5.3 Work Solution (Solution # 4)

This is a 10-fold dilution of Solution 3, and thus suited for ambient air PCB analysis. Equivalent concentrations may be obtained by dividing those values in Table 3.6 by 100.

## STANDARD SOLUTION #2

### STANDARD SOLUTION #2

EQUIVALENT CONCENTRATION AT 1.697 l/sec air flow

Syringe Setting "(ml/hr)"*	Calibrated Volume Delivered** "(ug/sec)"	(ng/m <sup>3</sup> )						Total Conc. (ng/m <sup>3</sup> )	Total PCB (ug) per minute at 1.679 l/sec
		Mono	DI	TRI	TETRA	PENTA	HEXA		
1	0.0567	60.50	41.00	57.83	74.79	62.51	140.37	437.0	0.044
2	0.0783	63.64	56.68	79.94	103.39	86.41	194.04	604.1	0.060
3	0.1175	125.46	84.96	119.92	155.09	129.61	291.07	1026.1	0.103
4	0.1642	175.28	112.79	107.54	216.68	181.09	406.67	1433.6	0.144
5	0.2408	257.14	174.26	245.79	317.88	265.65	596.58	1857.3	0.187
6	0.3458	369.25	250.24	352.95	456.46	381.47	856.69	2667.1	0.2699
7	0.5175	552.54	374.46	528.14	683.05	570.83	1281.93	4000.9	0.403
8	0.7308	780.31	528.82	745.86	964.63	806.15	1810.40	5636.2	0.568
9	1.1083	1183.37	801.98	1131.13	1462.89	1222.56	2745.53	8547.5	0.861
10	1.4417	1534.27	1043.17	1471.31	1902.85	1590.24	3571.25	9641.8	0.971
11	2.1083	2251.08	1525.56	2151.69	2782.79	2325.61	5222.69	16259.4	1.638

\*Nominal syringe setting.

\*\*Calibrated with a Hamilton 10 ml gas tight syringe using isoocatane.

TABLE 3.6

### 3.2.6. Optimization of PCB Wire Integrator by Adsorption/Desorption Time and Temperature.

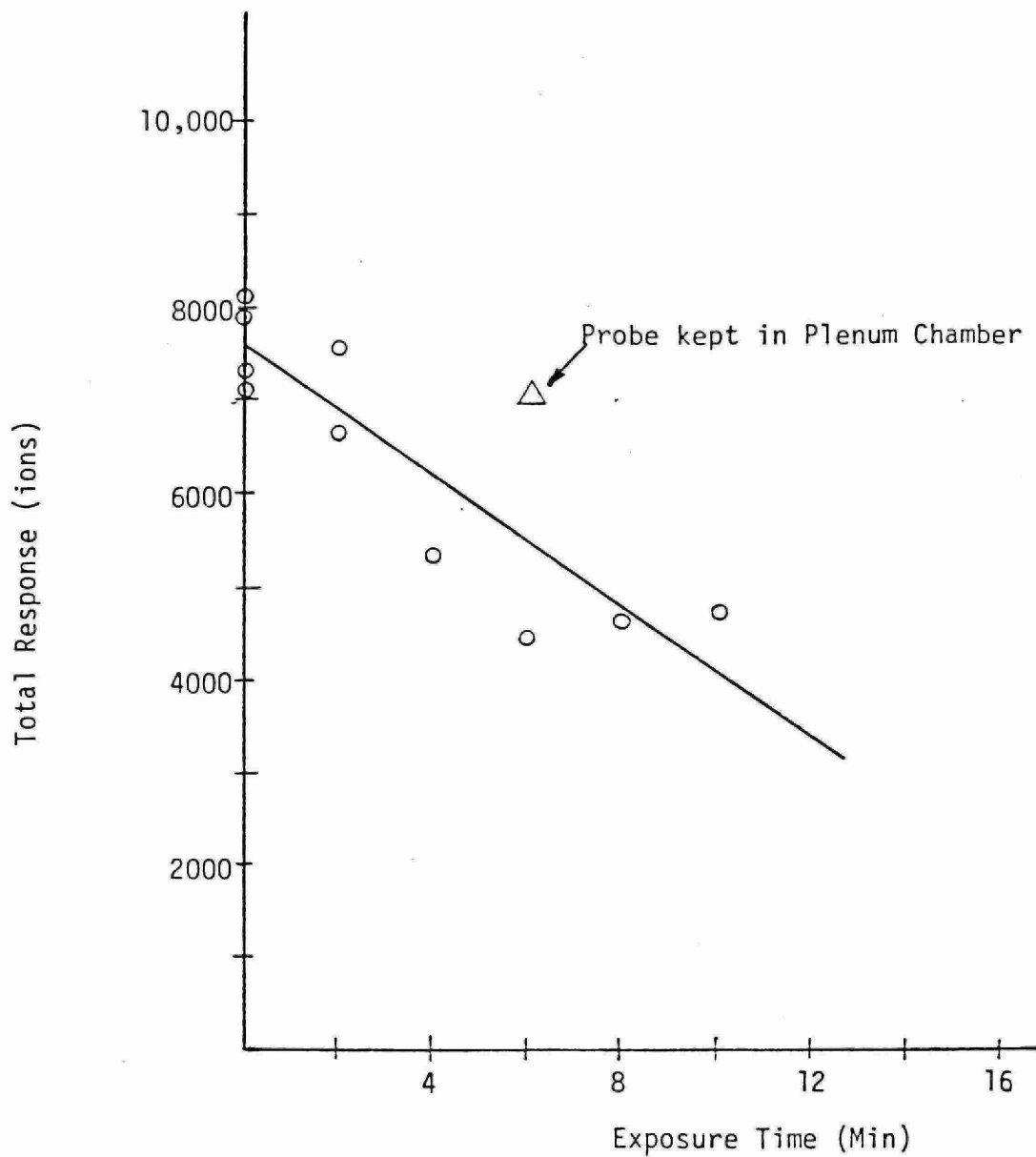
A partial optimization of the PCB wire integrator can be made by varying the sample collection (adsorption) time and sample desorption time, i.e. heating curve, to thermally desorb the trapped PCBs from the silicone film into the ionization zone. It is also important to optimize the sample collection temperature. In this section these important points will be discussed.

#### 3.2.6.1 Sampling Time.

The sample collection time is a very important factor, because the integrator's collection depends highly on the duration of the sampling. At the beginning of each collection cycle, the probe temperature is not due to the residual heat from the previous thermal desorption. PCBs do not adhere well on the silicone film when the probe temperature is hot. The probe is initially cooled with the sample air. As the probe temperature comes down, PCBs start to deposit on the silicone. However, when PCBs, which have deposited on the silicone for calibration, are exposed to the outdoor air stream, some of these PCBs tend to desorb at the sampling temperature (50°C). Figure 3.18 indicates this trend at 2 different temperatures. The results shown in this Figure were obtained by allowing PCB vapour, (approximately 28 ng/m<sup>3</sup>) from a constant vapor source (see Figure 3.7) to deposit on the PCB wire integrator for 2 minutes, then the PCB vapor valve was closed, and the PCB wire integrator was left in the adsorption position with the sample air flowing for 2, 4, 6, 8 and 10 minutes before a transfer of the integrator to the plenum chamber for thermal desorption. When this experiment was carried out, the temperature of the probe was not controlled, and was affected by the ambient temperature (33.8 - 34.4°C), resulting in some response fluctuation.

FIGURE 3.18 DESORPTION OF PCBs  
by Sample Air

$m/z = 256$   
Outdoor 33.8 - 34.4°C  
Van 31.1°C



Nevertheless, one can see loss in the TAGA responses due to the desorption of the PCBs which had been collected on the silicone film, but desorbed back to the air phase. In contrast, the PCBs on the probe do not desorb rapidly when the probe is kept in the plenum chamber, away from the sample stream. This is shown with the triangle in Figure 3.18. This difference may arise from the fact that the flow rate of the carrier gas in the plenum chamber is only 0.073 l/sec, whereas 1.7-2.5 l/sec of sample air is passed in the sampling line, i.e. 23-34 times more flow rate in the adsorption position than in the desorb position. This study was applied to monochlorobiphenyl through tetrachlorobiphenyl, and a similar trend was observed for all the species measured. This trend is drastic for monochlorobiphenyls and dichlorobiphenyls. However, as the molecular weight increases, this trend becomes smaller perhaps due to their low vapour pressures.

In the next experiment the probe was left in the adsorption position for 2, 6, 12, 20 minutes with a continuous flow of PCB vapor from an Aroclor 1248 constant source (See Fig. 3.7). After each sample collection, the PCB probe was immediately placed in the plenum chamber and heat was applied for the analysis. Figure 3.19 indicates Net Response versus sample collection time. One can see that the response is not linear with the sampling time, i.e., increasing the sampling time by 10 does not increase the TAGA<sup>TM</sup>3000 response by 10. This may be explained as follows:

- (1) the silicone film may be saturated very easily
- (2) the PCBs adsorb and desorb within a short period

Reason (1) may be a minor factor because the maximum load of trichloro-biphenyls applied over the period of 20 minutes was only 346 ng in this experiment, whereas in the stack gas analysis a much larger amount was

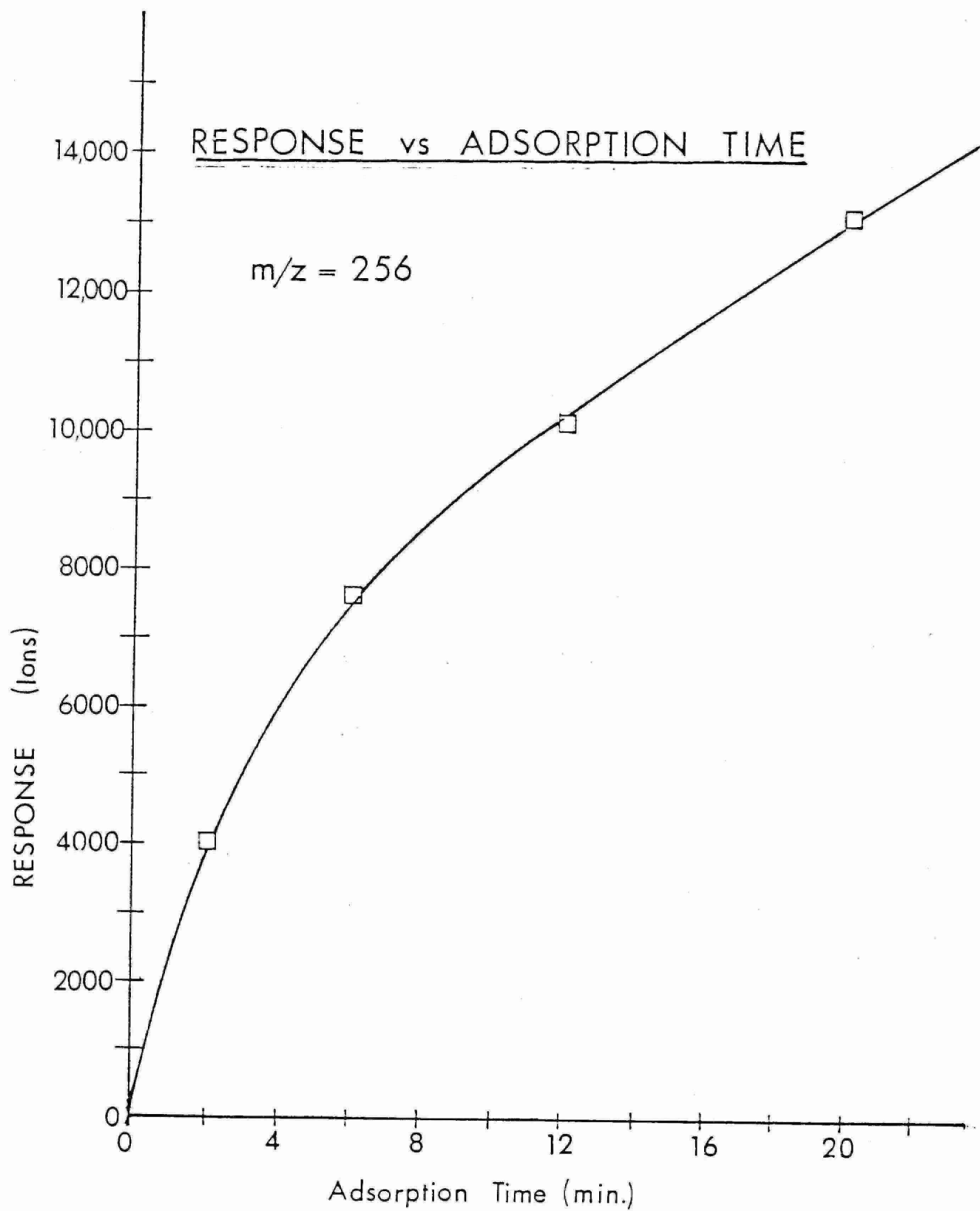


Figure 3.19

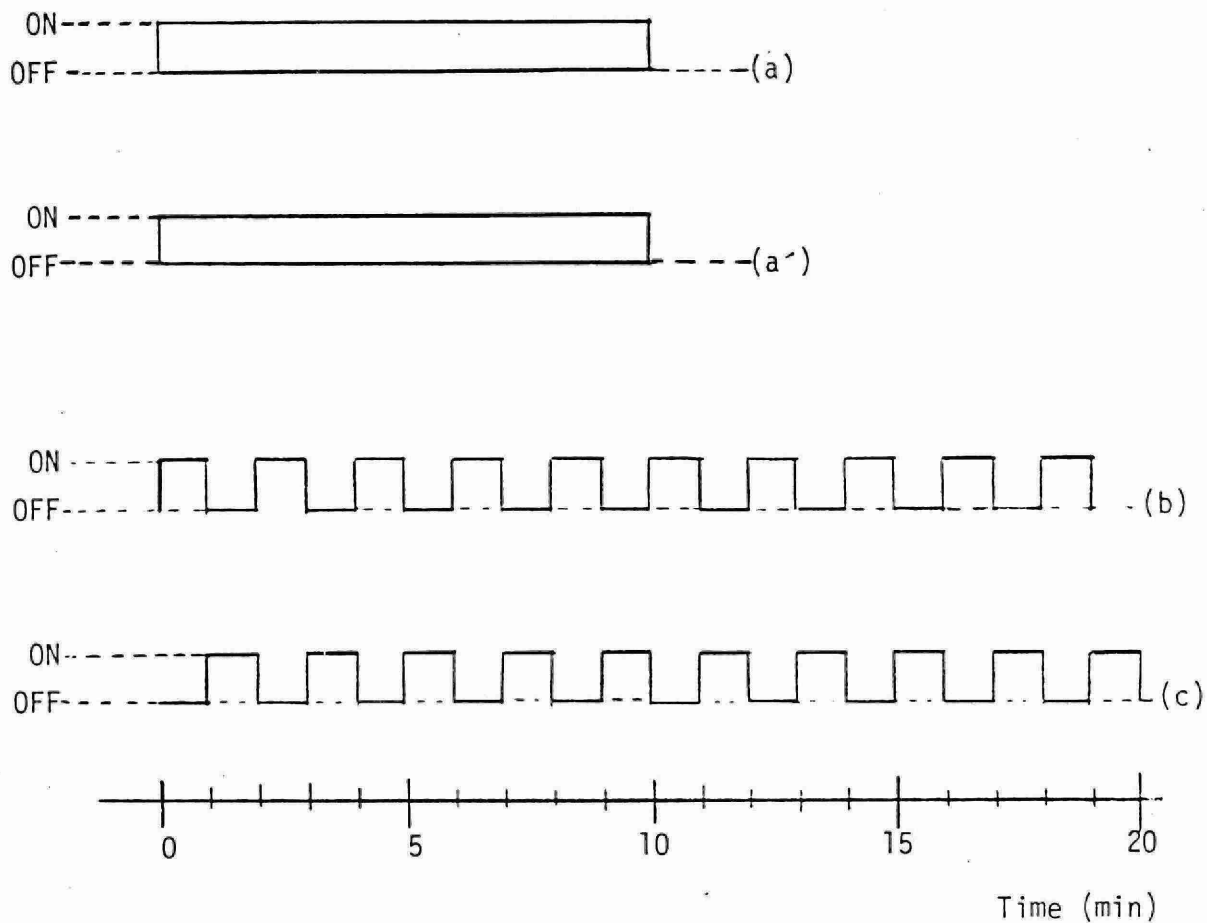
added to the system, and indicated a linear response over a wide range of PCB concentration, when all the sampling was carried out for 2 minutes.

In order to substantiate the second reason, two types of sample loading were tried. The first one was to leave the continuous PCB source valve open for 10 minutes. In the second the valve was opened for 1 minute, then closed for 1 minute. This step was repeated 9 times to produce the same amount of PCB discharge from the tank as in the first mode. As shown in Figure 3.20 the continuous application gave much higher responses (a and a') than the two repetitive runs. Since the same amount (approximately 28 ng/m<sup>3</sup>) of PCB vapor was applied to all the runs, the differences can be attributed to the partial desorption of the PCBs. This phenomenon was also observed for other masses, i.e., 36% loss at m/z = 166, 42% loss at m/z = 222, and 16% loss at m/z = 290.

After these experiments a sampling time of 2 minutes was adopted for the PCB monitoring.

#### 3.2.6.2 Sampling temperature.

The adsorption and desorption of PCBs on the PCB wire integrator are highly dependent on the temperature of the probe. In order to optimize the sampling temperature, a constant flow of PCB vapor was added to the system, using either a constant PCB source (See Fig. 3.7), or using a PCB standard solution via a heated glass inlet (Fig. 3.17). The temperature of the sample air is controlled by heating the glass tube upstream of the PCB wire integrator. The temperature is measured just downstream of the PCB integrator (See Fig. 3.14). Table 3.7 compares the system's net response to PCBs at various temperatures. The following observations have been made:



Mode	Net Response (ions)	Relative Response (%)
a	17157	100
a'	17497	
b	12327	71
c	11807	68

$A_v = 17327$

CONTINUOUS VERSUS REPETITIVE PCB APPLICATION

$m/z=256$        $28 \text{ ng/m}^3$

Figure 3.20



- (1) When the sampling temperature is high, low molecular weight PCBs do not adsorb well, especially mono- and di-chlorobiphenyls suffer.
- (2) However, when the sampling temperature is low, high molecular weight PCBs tend to deposit on the inner wall of the glass sampling line.

In order to optimize PCB transfer and adsorption, 50°C was chosen as the best temperature. The temperature is generally measured 1 minute after the start of each sampling cycle, since the temperature is initially higher due to the residual heat from the previous desorption step.

TABLE 3.7

Net Response to PCBs at Various Temperatures

M/Z	TEMPERATURE			
	45°	50°	55°	60°
188 (mono)	4890	3846	1348	1489
222 (di)	2653	1925	1609	1785
256 (tri)	1206	-	2857	1494
290 (tetra)	437	261	472	600
324 (penta)	129	119	-	138
362 (hexa)	98	89	53	69

#### 3.2.6.3. Sampling Flow

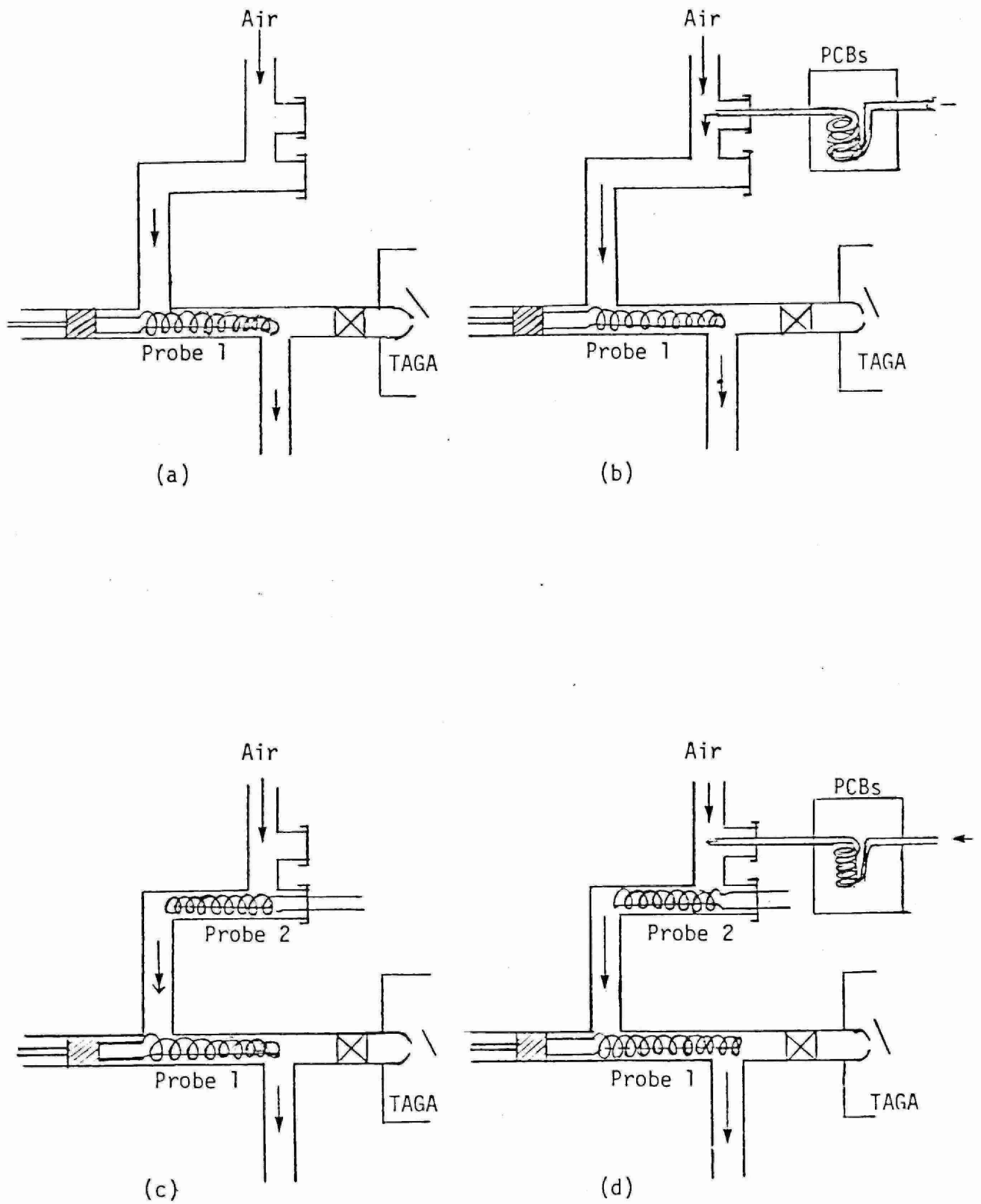
This topic has not been examined thoroughly. At the beginning of Phase I, our intention was to introduce as much sample air as possible to reduce sample memory effects. However, the design of the wire integrator (See Fig. 3.13) was simple at that time, and an increase in the sample flow often created pressure depression and the benzene vapor was drawn to the sampling side, resulting in response instability. It was also found that the behavior of the PCB wire integrator becomes abnormal under reduced pressure.

During Phase II the wire integrator system was modified to make it more vacuum tight. However, due to the lack of time, this experiment has not been repeated. Therefore, the sampling rate was set at 1.169 l/sec corresponding to 4.5" H<sub>2</sub>O depression across the critical orifice.

#### 3.2.6.4 Collection Efficiency of PCB Probe.

The determination of the collection efficiency of the PCB wire integrator can be determined as follows. Using only Probe 1, take a number of background readings as shown in (a) of Figure 3.21. Then, add a known amount (e.g., 42 ng/m<sup>3</sup>) of PCB vapor to the line as shown in (b) of Fig. 3.21. Obtain net response by subtracting the averaged background measured in (a) from the averaged total response in (b). This net response corresponds to the amount of PCBs added to the system (Net Response 1).

Then, insert a well conditioned probe (which is equivalent to Probe 1) into the sampling line upstream of Probe 1, as shown in (c) of Fig. 3.21. Probe 2 is electrically connected in parallel to Probe 1, so that the heating and cooling cycles of Probe 2 agree with those of Probe 1. Namely, when Probe



DETERMINATION OF PROBE COLLECTION EFFICIENCY

FIGURE 3.21

1 collects PCBs, Probe 2 also collects PCBs. In the same fashion, when heat is applied to Probe 1 in the plenum chamber, Probe 2 is also heated to drive off all the PCBs adsorbed on the silicone film on Probe 2. A number of background readings are made as in (c) of Fig. 3.21.

These background readings are generally lower than those observed in Step (a), because Probe 2 adsorbs a certain portion of contaminants present in air. After establishing stable background readings, the same amount of PCB vapor as in (b) is added to the system, shown in (d) of Fig. 3.21. The difference between the averaged response in Step (d) and averaged background in Step (c) is a net response of the instrument when a certain portion of the PCBs added to the system is trapped by Probe 2 (Net Response 2). Then, the following equation should indicate signal loss due to the trapping of the PCBs on Probe 2.

$$\begin{array}{l} \text{Signal} \\ \text{Loss} \end{array} \quad \epsilon = \frac{(\text{Net Response 1}) - (\text{Net Response 2})}{(\text{Net Response 1})} \times 100 (\%)$$

These two probes were switched later and very similar results were obtained. Table 3.8 is an example of calculations, when approximately 42 ng/m<sup>3</sup> of trichlorobiphenyls were added to the system using an Aroclor 1248 constant PCB vapor source (See Fig. 3.7). Probes 1 and 2 were coated with OV-17 and the initial computer program "DSORBA" was used to acquire the data. This software was a prototype, and the temperature control was not very accurate. This program has been replaced with PCBMON, thus giving a better control of the TAGA<sup>TM</sup>3000 data acquisition system. In view of the recent advances in the software and hardware, and interest in various GLC liquid phases, this experiment may be expanded to study various GLC phases at different flow rates, temperatures and concentrations.

Table 3.8 Example of Probe Efficiency Calculation

(See Fig. 3.21 for Probe positions)

Step (a) Probe 1, background

Readings (ions): 96, 475, -233, -18.3, 36.6

Average: 71.3 ,  $s_1 = 257.6$

Step (b) Probe 1, PCB Addition ca. 42 ng/m<sup>3</sup> trichlorobiphenyls

Readings (ions): 3401, 3447, 2953, 3474

Average: 3318.8,  $s_2 = 245.7$

(Net Response 1) = 3318.8 - 71.3 = 3247.5

Step (c) Probe 1, Background + Probe 2 in line

Readings(ions): -137.1, 45.7, -68.6, -34.7

Average: -48.7,  $s = 76.0$

Step (d) Probe 1 + Probe in line + PCB ca. 42 ng/m<sup>3</sup> trichlorobiphenyl

Readings(ions): 1829, 2085, 2336, 1966

Average: 2054.0  $s = 215.1$

(Net Response 2) = 2054.0 - (-48.7) = 2102.7

$$\epsilon = \frac{3247.5 - 2102.7}{3247.5} \times 100 = 35.3\%$$

Estimated Population Standard Deviation (Ref. 10)

$$\hat{\sigma} = \sqrt{\frac{5 \times (257.6)^2 + 4 \times (245.7)^2 + 4 \times (76.0)^2 + 4 \times (215.1)^2}{5 + 4 + 4 + 4 - 4}} \times \sqrt{\frac{4-1}{4}}$$

$$= 212 \div 3247.5 \times 100 = 6.5\%$$

$$\epsilon = 35.3\% \pm 6.5\%$$

### 3.3            PCB CALIBRATION' SENSITIVITIES' DETECTION LIMITS AND RESPONSE CHARACTERISTICS.

#### 3.3.1            PCB Vaporization Methods for Calibration

The current calibration method has been briefly explained in Section 3.2.4. This section is dedicated to review several calibration techniques tested in the past.

The ideal procedure for calibration a system with measures gas phase concentrations is to produce under normal sampling conditions several different concentrations of the compound of interest in the air and record the response to each concentration. A calibration curve of response versus concentration can be drawn, and unknown values in the concentration range covered by the curve can be interpolated. Known concentrations can often be conveniently produced from a solid or liquid sample by injecting equilibrated head space vapor into a carrier at known rates. Unfortunately, this method cannot be used with PCBs because of the lack of vapor pressure data for the various PCB components.

Therefore, calibration procedures have been developed which rely on the vaporization of a known mass of PCB into the air carrier to produce a known concentration.

##### 3.3.1.1            Tungsten Wire Probe

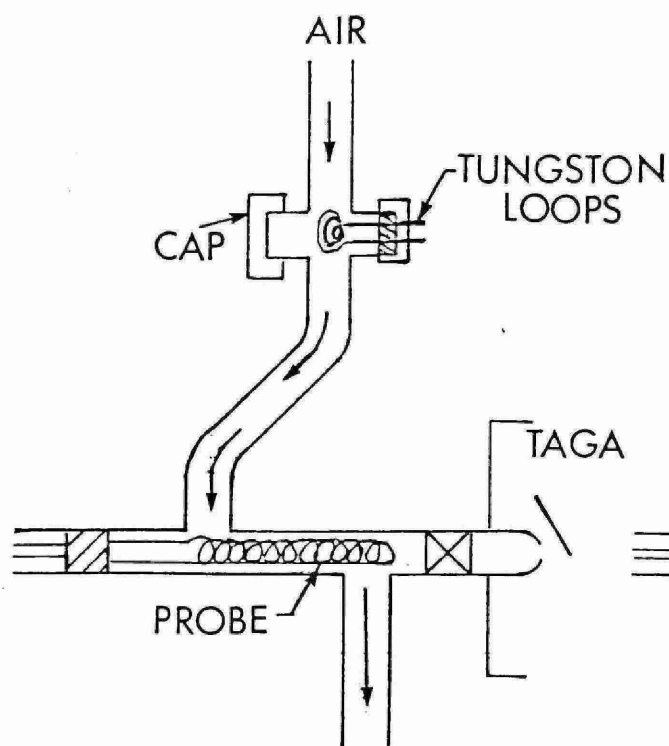
This system had been originally developed to calibrate the Aroclor constant PCB vapor source (See Ref. 6, Section 6.1), because of the lack of vapor pressure data for the various constituents. This system

is illustrated in Figure 3.22, (a) and (b). This involves a small tungsten wire probe (5-14 mm diameter loops), supported in the sampling line either in the vertical (a) or horizontal position (b). Air is drawn past the probe into the PCB integrator region by the air motor. The cap is opened and a drop of the PCB standard solution prepared in Section 3.2.5 is placed on the tungsten loops with a micro-syringe. The cap is closed, the solvent (iso-octane) is evaporated, and the wire is heated with a voltage pulse (1-3V). This vaporizes the PCBs on the loops into the air stream within a very short period of time (typically less than 1 second). The air flow rate of 1.5 -2.5 l/s produces turbulent flow and ensures that the sample is mixed in the carrier by the time it reaches the PCB integrator.

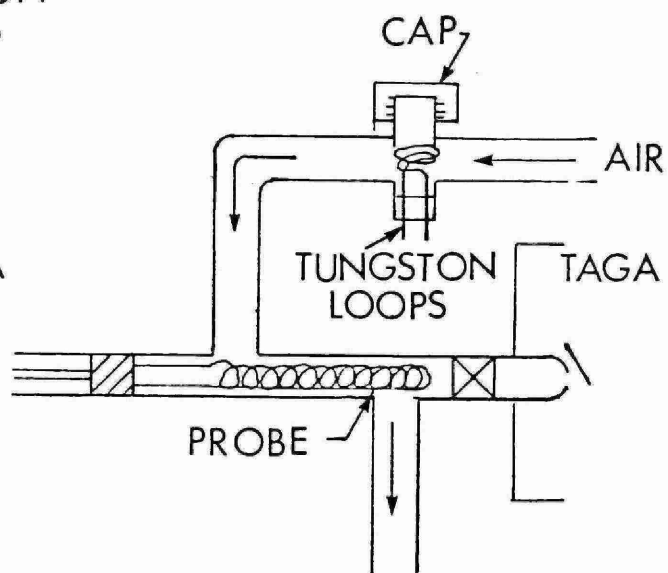
Although this method was useful in the SCIEX laboratory, it did not produce reproducible results in the van for the following reasons:

- (1) Because of the limited space in the van, it was difficult to place the tungsten loops on the same horizontal plane as the PCB integrator. The best results were obtained in the laboratory, when these two wires are oriented in parallel on the same horizontal plane.
- (2) Because of the continuous vibration caused by the van power generators, a drop of the standard often fell down before the solvent evaporates, thus making the quantitation difficult.
- (3) The air at the high flow rate often blew away the drop on the tungsten wire.

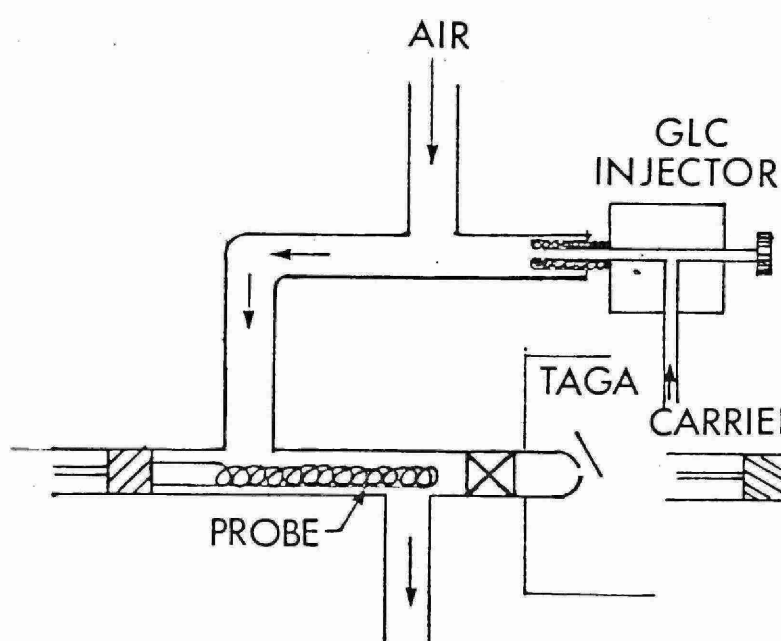




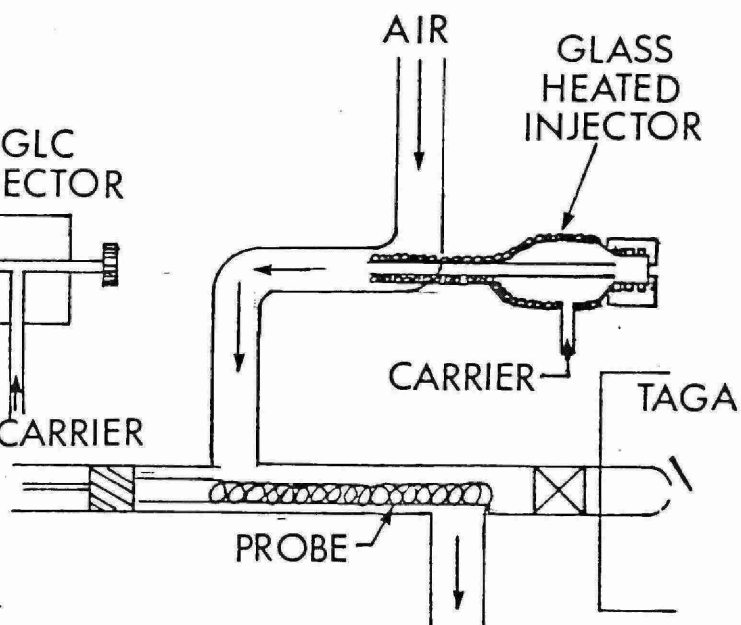
(a)



(b)



(c)



(d)

# CALIBRATION METHODS TESTED

Figure 3.22

In order to give a wider surface area, a tungsten ribbon and a platinum ribbon, both approximately 4 mm wide x 1 mm thickness were examined in place of the tungsten loops. However, both were found to be very elastic and electro-conducting resulting in a short circuit of several fuses. For these reasons this approach was abandoned.

#### 3.3.1.2 Heated Liquid Injectors.

In order to overcome the difficulties encountered with the tungsten loops, a heated liquid injector was examined to vaporize PCBs. Model (c) in Figure 3.22 is a prototype. A GLC injector was examined to introduce PCB vapors into the sample line. The injector was heated at 300°C - 350°C, and an aliquot of the standard solution was injected. This proved to be a considerable improvement over the previous models (a) and (b). However, this injector is made of metal, and an all glass heated injector was a better choice than stainless steel or copper. So, model(d) in Figure 3.22 was designed and fabricated. This is also illustrated in Fig. 3.17. In this system a known aliquot of the standard solution is injected through a septum (high temperature) into the glass tube which is heated at 350°C and a gentle stream of the carrier (prepurified air or nitrogen) carries the vaporized PCBs into the PCB wire integrator region.

Initially, manual or pulsed injections were tried, but it was found that continuous injection with the use of a motorized syringe drive produce much better reproducibility. This observation may result from the desorption phenomenon discussed in Section 3.6.1. It is difficult to reproduce each manual injection in the field mode of operation. Thus, it is simpler and more accurate to leave the motorized syringe drive running for 2 minutes of each sampling,

than, injecting 2, 3, 4, 5, ....., 10  $\mu$ l of the standard exactly at the middle of the sampling period.

### 3.3.2 Calibration Procedure

An all glass heated injector (Fig. 3.17) was installed in the sampling line approximately 1 m upstream of the integrator (Fig. 3.16). Aliquots of dilute PCB solutions (prepared in Section 3.2.5.2) of varying but known concentrations were injected through the port using a syringe drive (SAGE Instrument, Model 341). A calibration of the system's response in units of ions collected during the thermal desorption at the  $m/z$  of interest is made by comparing with quantity of an individual PCB species added to the sample line to produce equivalent ambient or stack concentration. If the collection efficiency of the integrator is independent of concentration (which has been confirmed and will be shown later), then the total mass injected can be divided by the total volume of air sampled during a two-minute collection to convert the calibration from ions per unit mass per unit equivalent concentration (See Section 3.2.5.2. for detail).

The total responses, i.e., background ion count value plus added PCB value, are plotted against the calculated equivalent atmospheric (or stack) PCB concentration to determine the background (intercept value), and sensitivity (ions/ng/ $m^3$ ) and detection limit (ng/ $m^3$ ) by the "Least Squared Curve Fitting" method.

The method of least squares is often used in statistics to avoid individual judgement in constructing lines, parabolas or other approximating curves to fit sets of data. Consider Figure 3.23 in which

the data points are given by  $(X_1, Y_1)$ ,  $(X_2, Y_2)$ ,  $(X_3, Y_3)$  ...  $(X_n, Y_n)$ . For a given value of  $X$ , say,  $X_1$ , there will be a difference between the value  $Y$ , and the corresponding value as determined from the curve  $C$ . As indicated in the figure we denote this difference by  $D_1$ , which is sometimes referred to as a deviation, error or residual and may be positive, negative zero.

Similarly, corresponding to the values  $X_2, X_3$  ...,  $X_n$  we obtain the deviations  $D_2, D_3$  ...  $D_n$ . A measure of the "goodness of fit" of the curve  $C$  to the given data is provided by the quantity  $D_1^2 + D_2^2 + \dots + D_n^2$ . If this sum is small, the fit is good. If it is large, the fit is poor. That is, all curves approximating a given set of data points, the curve having the property that  $D_1^2 + D_2^2 + \dots + D_n^2$  is a minimum is called a "best fitting curve". A curve having this property is said to fit the data in the least square sense and is called a least square curve. Thus a line having this property is called a least square line. A parabola with this property is called a least square parabola, etc. (Reference 11).

It is customary to employ the above definition when  $X$  is the independent variable (equivalent PCB concentration) and  $Y$  is the dependent variable (TAGA response in ions). The least square line approximating the set of points  $(X_1, Y_1)$ ,  $(X_2, Y_2)$ ,  $(X_3, Y_3)$  ...  $(X_n, Y_n)$  has the equation

$$Y = a + b X$$

where the constants  $a$  and  $b$  are determined by solving simultaneously the equations

$$\sum Y + aN + b \sum X$$

$$\sum XY = a \sum X + b \sum X^2$$

and  $N$  is number of items in the data (i.e., total frequency). These two

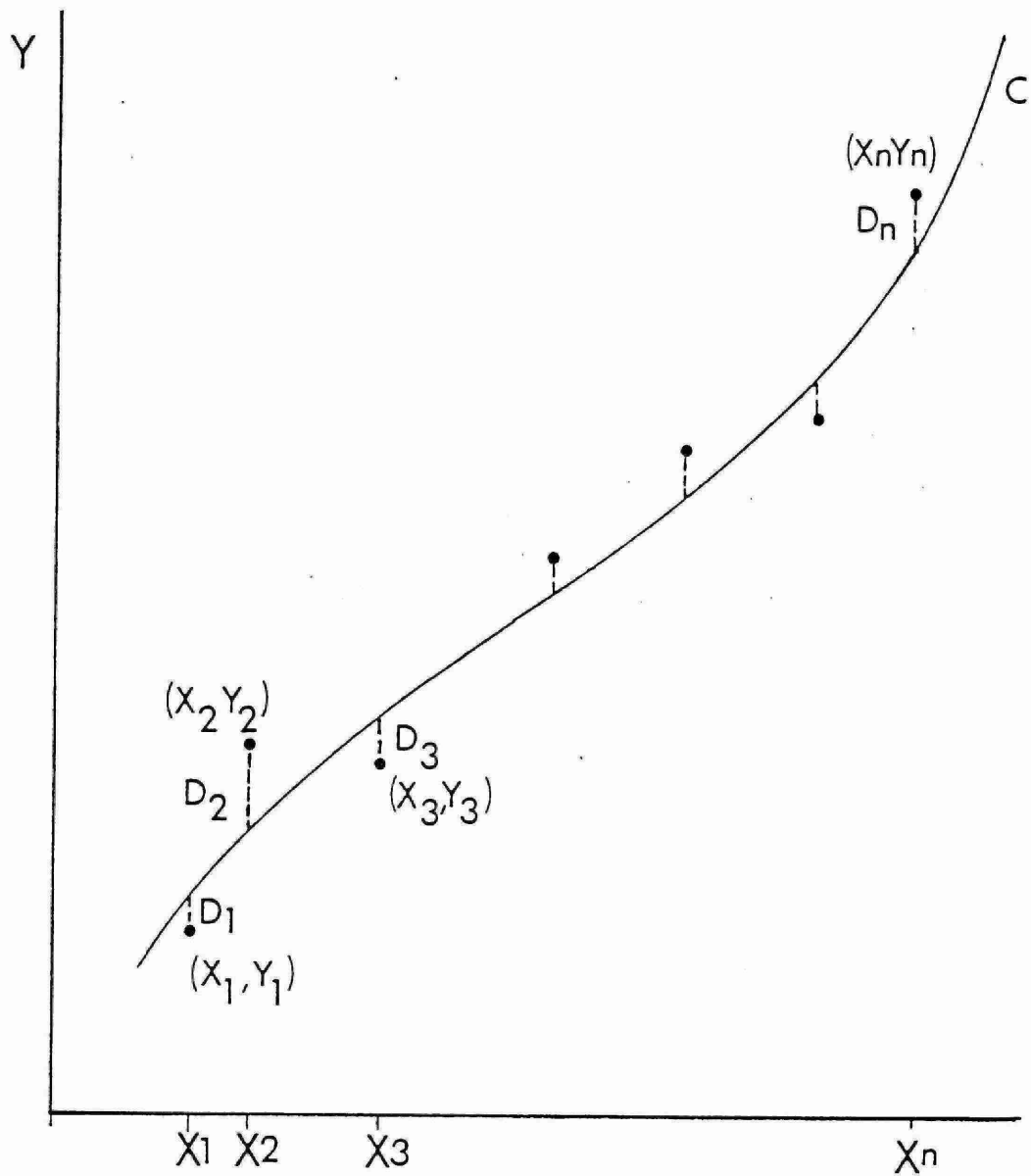


Figure 3.23 LEAST SQUARE CURVE

formulas are called the "normal equations for the least square line". The constants a and b can be found from the formulas:

$$a = \frac{(\sum Y)(\sum X^2) - (\sum X)(\sum XY)}{N \sum X^2 - (\sum X)^2}$$

$$b = \frac{N \sum (XY) - (\sum X)(\sum Y)}{N \sum X^2 - (\sum X)^2}$$

The intercept is the background reading when no PCBs are added, and the slope b is the system's sensitivity.

Table 3.9 is an example of a calibration using charcoal-filtered ambient air. The first column indicates row numbers for the tabulation. The middle column lists total responses in ion counts and the last column is a list of equivalent atmospheric concentrations in (ng/M<sup>3</sup>). This calculation was done by the computer program PCBGGEN to compute the intercept a, sensitivity (slope) b, and the linear correlation coefficient r. The linear correlation coefficient will be discussed in the next chapter in detail. Figure 3.24 is a plot of the total response versus equivalent atmospheric concentration of the monochlorobiphenyl. The slope and intercept of the line in the figure were obtained from the above computation.

### 3.3.3 Detection Limit

During Phase I it was observed that background fluctuations due to interfering chemicals present in the atmosphere cause most of the variation in the repeated observations. Table 3.10 is an example of a

typical outdoor air observed in summer in a light industrial area (Thornhill, Ontario where SCIEX is located). By mutual agreement between SCIEX INC. and the Ministry's scientific advisors the detection limit has been defined as the equivalent atmospheric (or stack) concentration corresponding to  $3s$  of the background readings, where  $s$  is the standard deviation (See Ref. 10 or 11).

The standard deviation,  $s$ , is the most popular measure of variability in the data. It measures the scatter of data in terms of differences from the mean value. As such it affords us with a quantitative measure of variability rather than the positional measures of the various range values. The units of a standard deviation will be those of the original observations, i.e., ion counts which is a definite advantage.

In the process of calculating the standard deviation we first determine the so-called "variance", which itself is a measure of variability and in certain situations preferable over the former. If  $X$  is the variable and we have  $N$  observations on its value, then the variance, denoted by  $s^2$ , is computed according to the following rule.

Table 3.9

Example of Calibration Using  
Charcoal-Filtered Ambient Air (March 13, 1980)

TOTAL RESPONSE VS CONCENTRATION MONOCHLOROBIPHENYL

<u>Row</u>	<u>1(188)</u>	<u>2(ng/m<sup>3</sup>)</u>
1	129 ions	0
2	123	0
3	127	0
4	148	0
5	130	0
6	119	0
7	144	0
8	123	0
9	355	22.51
10	361	22.51
11	434	22.51
12	428	22.51
13	369	22.51
14	360	22.51
15	291	22.51
16	255	11.81
17	293	11.81
18	265	11.81
19	228	5.53
20	193	5.53
21	246	5.53
22	200	2.57
23	204	2.57
24	249	2.57
25	228	2.57
26	219	2.57

For column 1 versus column 2

Slope 9.77347

Intercept 155.653

Corr. Coef. 0.931091

M/Z	3S	Detection Limit
188	31.0 ions	3.173 ng/m <sup>3</sup>



TABLE 3.10

Example of Background Fluctuation in Thormhill, Ont.

<u>Time</u>	<u>mono</u>	<u>188</u>	<u>190</u>	<u>di</u>	<u>222</u>	<u>224</u>
10:03		5882	5966		7257	7614
10:08		5951	5734		6641	6890
10:13		6300	4758		7463	7421
10:15		6704	5126		7714	7778
10:18		5438	4031		6269	6388
10:21		5242	3873		5929	5864
13:50		3282	2967		4398	4548
13:52		3183	2840		4040	4257
15:16		4835	4880		7301	7747
15:19		3906	3470		5437	5466
15:22		4037	3542		5686	5773
15:26		3455	2861		4718	4922
15:30		3365	2966		4755	4759
15:33		3870	3539		4609	5590
15:43		3854	3490		5604	5628
17:06		3253	3362		4567	4533
17:14		2166	2119		2892	2818
17:25		2254	2175		3108	3143
	<u>tri</u>	<u>256</u>	<u>258</u>	<u>tetra</u>	<u>290</u>	<u>292</u>
10:25		2683	2321		1047	991
10:28		2942	2641		1116	1052
10:34		3364	2866		1196	1242
13:26		2442	2346		964	1056
13:28		1906	1848		828	885
13:33		2579	2283		820	998
13:35		2410	2044		799	809
16:42		2651	2186		983	981
16:45		2397	2131		970	980
18:29		1195	1017		457	496
18:33		1096	913		444	499
18:40		1136	1124		511	532
18:48		1219	960		470	512
18:55		1213	1153		535	534
	<u>penta</u>	<u>323</u>	<u>325</u>	<u>hexa</u>	<u>357</u>	<u>361</u>
10:40		633	740		329	350
10:42		609	755		367	420
10:46		644	740		355	438
10:50		675	830		326	385
13:13		602	793		336	341
13:15		750	948		412	373
13:19		671	812		337	33
13:23		721	864		308	342
15:56		713	882		312	335
15:59		594	719		254	339
16:51		554	652		233	295
18:58		286	349		192	207
19:05		382	411		197	209
19:12		243	290		128	128
19:22		238	305		141	162

$$(\text{Variance,}) s^2 = \frac{\sum (X - \bar{X})^2}{N}$$

This rule says that we are to subtract the mean value of the data, denoted by  $\bar{X}$ , from each individual observation, square these differences, sum all of them, and then divide this total by the number of observations involved. The standard deviation is just the positive square root of the variance, and logically denoted by  $s$ .

$$s = \sqrt{\frac{\sum (X - \bar{X})^2}{N}}$$

At this point we should introduce our modification to the above calculations which has to do with the fact that for certain purposes the value we calculate from the above rules, for the variance and standard deviation, would in a sense be "biased". As long as we are talking about the data set itself, then the rules given above apply. It is when we wish to assign the data variance or standard deviation over to the underlying process giving rise to the data that we must introduce a correction factor which will correct the bias. We simply multiply the variance as calculated with the above rules by the quantity  $N/(N-1)$ , or, the calculated standard deviation by the factor  $\sqrt{N/(N-1)}$ . When  $N$  is fairly large the bias will be minimal, and therefore we do not usually use the factor when  $N$  is greater than 30.

Since our observations were, in general, less than 30. The following equation has been used throughout this program:

$$s = \sqrt{\frac{N \sum (X^2) - (\sum X)^2}{N(N-1)}}$$

$X$  = variable

$N$  = number

For instance, 8 background readings were recorded for  $m/z = 188$ . (See Table 3.9). These are 129, 123, 127, 148, 130, 119, 144 and 123 ions, respectively.

$$\bar{X} \text{ (mean)} = 130.4; s = 10.3, 3s = 31.0$$

$$\text{Detection Limit} = \frac{3s}{\text{slope}} = \frac{31.0}{9.77} = 3.17 \text{ ng/m}^3$$

$$\text{slope } 9.77$$

This is shown at the bottom of Table 3.8.

### 3.3.4 Isotopic Abundance Ratio

A "chemically" pure organic compound will give a mixture of mass spectra because the elements which compose the compound are not isotopically pure. (Reference 12). PCBs are composed of carbon, hydrogen and chlorine atoms. The natural isotopic abundances of these elements are as follows (Ref. 13):

$^1\text{H}$ : Mass 1.007825, 99.985% Natural Abundance

$^2\text{H}$ : Mass 2.0140, 0.015% Natural Abundance

$^{12}\text{C}$ : Mass 12.00335, 98.89% Natural Abundance

$^{13}\text{C}$ : mass 13.00335, 1.11% Natural Abundance

$^{35}\text{Cl}$ : Mass 34.96885, 75.53% Natural Abundance

$^{37}\text{Cl}$ : Mass 36.96590, 24.47% Natural Abundance

The abundance resulting from combinations of several isotopes of the same element can be calculated from the binomial expansion

$$(a+b)^n = a^n + na^{n-1}b + n(n-1)a^{n-2}b^2/2! + n(n-1)(n-2)a^{n-3}b^3/3! + \dots$$

where  $a$  is the relative abundance of the first isotope, e.g. 1.00 for  $^{35}\text{Cl}$ ,  $b$  the relative abundance of the second isotope, e.g., 0.25 for  $^{37}\text{Cl}$ , and  $n$  is the number of atoms. Thus, for a peak containing 3 chlorine atoms, the abundance of the  $(M+2)^+$  peak relative to the  $M^+$  peak should be

$3 \times (1)^2 \times (0.325) = 0.975$ . Table 3.10 is a compilation of calculations applied to various combinations of  $^{35}\text{Cl}$  and  $^{37}\text{Cl}$  atoms. The carbon-13 isotope contained in the 12 carbon atoms of the PCB molecule will give rise to

$M^+$	100%	$M^+$ : monisotopic peak, i.e., the peak containing the most abundant isotopes of the elements forming the compound in question.
$(M+1)^+$	13.2%	
$(M+2)$	0.80%	

The  $^2\text{H}/^1\text{H}$  ratio is so low that the contribution of the  $^2\text{H}$  can be ignored. Please note that neither  $^{13}\text{C}$  nor  $^2\text{H}$  contribution has been accounted for in preparing Table 3.10.

Table 3.11

Natural Abundances of Combinations of Chlorine Isotopes in PCBs

Formula	Mass (M)	RELATIVE ABUNDANCES (%)									
		M	M+2	M+4	M+6	M+8	M+10	M+12	M+14	M+16	M+18
C <sub>12</sub> H <sub>8</sub> Cl <sub>2</sub>	222.0	100	65.0	10.6							
C <sub>12</sub> H <sub>7</sub> Cl <sub>3</sub>	255.96	100	97.5	31.7	3.4						
C <sub>12</sub> H <sub>6</sub> Cl <sub>4</sub>	289.82	76.9	100.0	48.7	10.5	0.9					
C <sub>12</sub> H <sub>5</sub> Cl <sub>5</sub>	323.88	61.5	100.0	65.0	21.1	3.4	0.2				
C <sub>12</sub> H <sub>4</sub> Cl <sub>6</sub>	357.84	51.2	100.0	81.2	35.2	8.5	1.1	0.06			
C <sub>12</sub> H <sub>3</sub> Cl <sub>7</sub>	391.80	43.9	100.0	97.5	52.8	17.1	3.3	0.36	0.02		
C <sub>12</sub> H <sub>2</sub> Cl <sub>8</sub>	425.77	33.8	87.9	100.0	65.0	26.4	6.8	1.1	0.10		
C <sub>12</sub> HCl <sub>9</sub>	459.73	26.3	76.9	100.0	75.9	36.9	12.0	2.6	0.36	0.03	minute
C <sub>12</sub> Cl <sub>10</sub>	493.69	21.0	68.3	100.0	86.6	49.2	19.2	5.2	0.97	0.12	0.01

In a strict sense has to compute the abundances of the PCB isotopic peaks by  $(a+b)^l(c+d)^m(e+f)^n$  where a,b,c,d,e and f are the natural abundances of  $^{12}\text{C}$ ,  $^{13}\text{C}$ ,  $^1\text{H}$ ,  $^2\text{H}$ ,  $^{35}\text{Cl}$  and  $^{37}\text{Cl}$ ; l, m, n refer to the numbers of carbon, hydrogen and chlorine atoms in each PCB species. However, only the two most abundant peaks were monitored for each PCB species containing the same number of chlorine atoms. The  $M^+$  and  $(M+2)^+$  peak intensities were measured for dichlorobiphenyl through pentachlorobiphenyl. Only the  $M^+$  peak was measured for monochlorobiphenyls. The  $(M+2)^+$  and  $(M+4)^+$  peaks were selected for hexachlorobiphenyls, because the abundance of the  $M^+$  is smaller than those of  $(M+2)^+$  and  $(M+4)^+$ , when six chlorine atoms are attached to the biphenyl ring system. The contribution of  $^{13}\text{C}$  to the  $(M+2)^+$  peaks is less than 1% of the most abundant peaks. Therefore, those values tabulated in Table 3.10 were used to evaluate the PCB analysis data described in this report. Since peak heights in the spectra are proportional to the number of ions at each m/z, relative abundances can be calculated from measured peak intensities, i.e., sensitivity of the instrument to the PCBs. For instance, the MOE TAGA<sup>TM</sup>3000 unit produced the following sensitivities to a known amount of trichlorobiphenyl added to ambient air in a light industrial area.

<u>m/z</u>	<u>Sensitivity (ions/ng/m<sup>3</sup>)</u>
256	51.0
258	46.4

The ratio 46.4/51.0 gives 0.92, and this is the observed isotopic abundance ratio. As shown in Table the  $(M+2)^+/M^+$  ratio of trichlorobiphenyl is 0.975. If this observed ratio agrees with the theoretical ratio one can be sure that these peaks are due to PCB species. However, any large deviation between these two

ratios would suggest the presence of interfering chemicals and the data should be handled with care. Because the atmospheric environment harbors a great number of chemicals as a result of anthropogenic as well as natural activities, many compounds can appear at the same  $m/z$  values as PCBs.

It is therefore very important to compare the theoretical isotopic abundances to the ratios of the TAGA<sup>TM</sup> responses. This subject will be further discussed in the subsequent chapters.

#### 4. STATISTICAL ANALYSIS AND COMPUTER SOFTWARE DEVELOPMENT

While Phase I was underway, the use of statistical analysis to evaluate the PCB data obtained by the TAGA<sup>TM</sup> unit and the development of computer programs were felt necessary to the TAGA<sup>TM</sup> operators for the reasons described in the following section.

##### 4.1 Rational for Use of Statistical Analysis.

The analysis of PCBs in the environment is one of the most difficult and challenging tasks for the environmental scientist. As mentioned in Section 2.2 PCBs present in the environment are a complex mixture of many chlorinated biphenyls. There are also many pollutants which appear at m/z of PCBs in the mass spectrum. As has been shown in Table 3.9, the TAGA<sup>TM</sup> registered response fluctuations due to changing chemical noise. It is therefore important to distinguish PCB signals from background chemical noise.

In order to evaluate the "goodness of TAGA<sup>TM</sup> response" to PCBs, it is important to evaluate a measure of the proportional association between the TAGA response and the amount of PCBs added to the sample line. Also, associations between the TAGA responses at various m/z values of PCBs are a good measure to evaluate the presence of PCBs in the sample air.

##### 4.2 Rational for Computer Program Development

When the PCB analysis was carried out with TAGA<sup>TM</sup>2000 units, these instruments were not equipped with the proper computer programs to process PCB signals. Therefore, the PCB analysis was made by desorbing the collected PCBs on the wire integrator and monitoring at one m/z value. So, if one needed basic information on the atmospheric concentration of monochlorobiphenyls



through hexachlorobiphenyls, one would have to repeat this 3-4 minute process for at least 5 times. In order to monitor 2 peaks per each PCB species containing the same number of chlorine atoms, the adsorption/desorption cycle had to be repeated 12 times, thus, requiring a minimum of 36 minutes per set of data. The TAGA<sup>TM</sup>2000 system at that time was not equipped with a computer program to reduce the PCB data obtained by the adsorption/desorption process. The system response, expressed in a peak area, had to be manually counted and converted into concentration. Neither computer control of the TAGA<sup>TM</sup> ion optics nor multiple selected ion monitoring was possible.

These short-comings were a great burden in developing PCB analytical methods by the use of the MOE TAGA<sup>TM</sup>3000 unit.

Although the first generation TAGA computer program was available at the time of the van delivery, the program was to facilitate the basic use of the TAGA<sup>TM</sup>3000 unit for acquisition of ambient air mass spectra in the real time analysis mode.

In order to optimize the instrument's parameters, to speed up data acquisition and reduction, it was an absolute necessity to develop computer programs dedicated to the PCB data acquisition and reduction.

#### 4.3 Statistical Analysis

The importance of statistical analysis to obtain reliable results from the raw data produced by the MOE TAGA<sup>TM</sup>3000 unit will be shown by the linear correlation coefficient between the TAGA<sup>TM</sup> responses, and the response and concentration of PCBs added to the sample line.

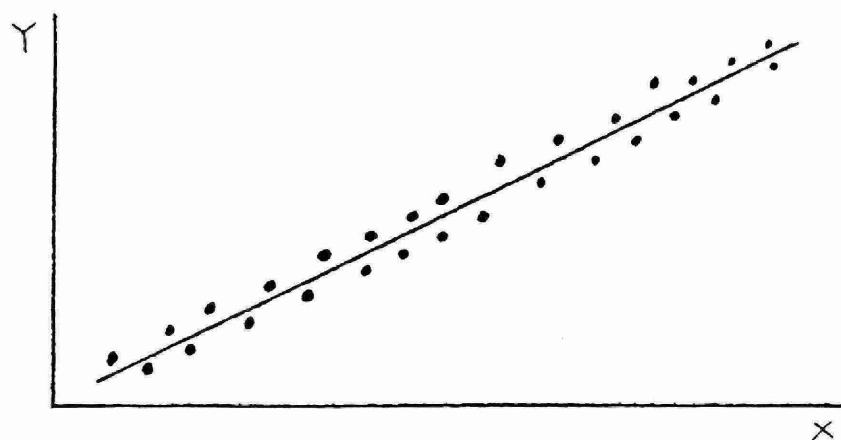
If X and Y denote the two variables under consideration, e.g., concentration of PCBs and TAGA response, or TAGA responses at different m/z values of interest, a scatter diagram shows the location of points (X,Y) on a rectangular coordinate system. If all points in this scatter diagram lie near a line, as in (a) and (b) of Figure 4.1., the correlation is called linear. By the word "linear" we mean that the formula expressing the nature of the relationship between X and Y is that of a straight line,  $Y=A+BX$ . If Y tends to increase as X increases, as in (a), the correlation is called positive or direct correlation. If Y tends to decrease as X increases, as in (b), the correlation is called negative or inverse correlation. If there is no relationship indicated between the variable, as in (c), there is no correlation between them, i.e., they are uncorrelated.

If the TAGA response (Y) tends to increase as PCB concentration (X) increases, we say that the TAGA response is due to the added PCBs. However, if the scatter diagram follows (b) or (c), then the TAGA responds to interfering chemicals as well as the added PCBs, and we cannot quantitate PCBs accurately.

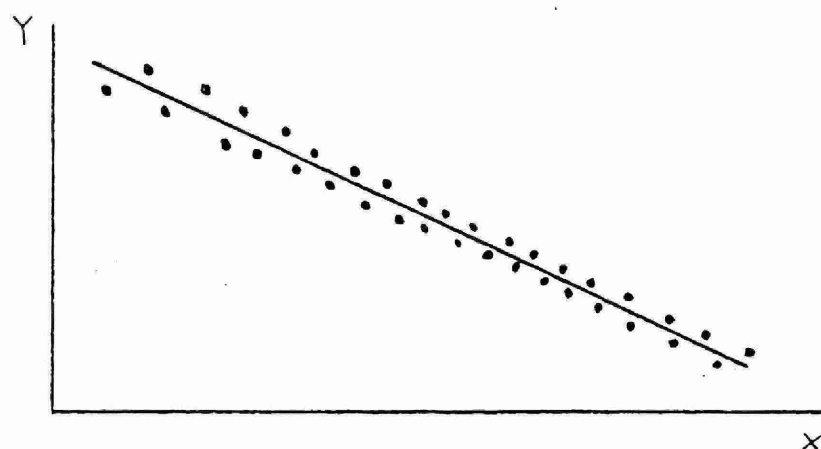
As mentioned in Section 3.3.4 PCB species containing m chlorine atoms produces m + 1 mass spectral peaks. The isotopic ratio of these peaks is independent of its concentration in the sample, responses at the isotopic peaks of interest should increase or decrease in the proportional fashion according to their isotopic ratio. However, if the sample air is contaminated with interfering chemicals, this proportionality would not hold.

Another important point is the fact the PCBs are a mixture of biphenyls substituted with various numbers of chlorine atoms (See Table 3.1.).

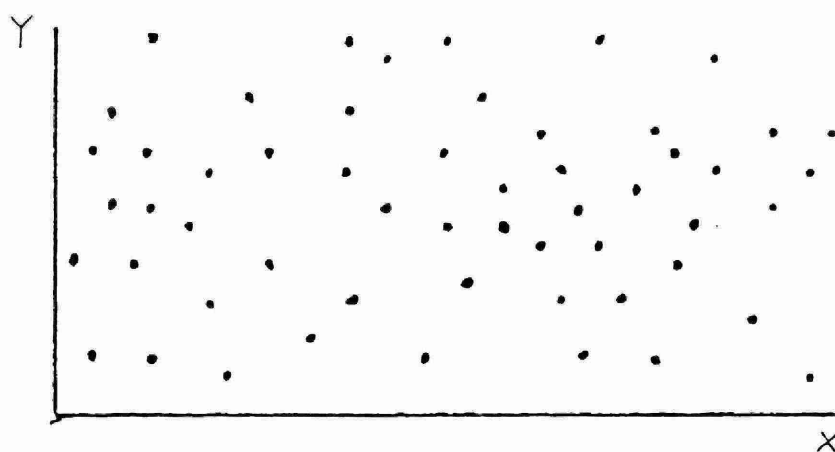
FIGURE 4.1 CORRELATIONS



(a) Positive Correlation



(b) Negative Correlation



(c) No Correlation

This means that if the atmospheric concentration of trichlorobiphenyls increases, the concentration of tetrachlorobiphenyls usually tends to increase. Thus, the TAGA responses for different PCB species should increase or decrease in a proportionate fashion, if the mass spectra are free from interfering chemical noise.

In statistics the total variation of the variable Y is defined as  $\Sigma(Y-\bar{Y})^2$ , i.e., the sum of the squares of the deviations of the values of Y from the mean  $\bar{Y}$ .

$$\Sigma(Y-\bar{Y})^2 = (Y-Y_{est})^2 + (Y_{est} - \bar{Y})^2$$

The first term on the right hand side of the above equation is called the "unexplained variation" while the second term is called the "explained variation", so called because the deviations  $(Y_{est} - \bar{Y})$  have a definite pattern while the deviations  $(Y-Y_{est})$  behave in a random or unpredictable manner. Similar results hold for the variable X.

The ratio of the explained variation to the total variation is called the coefficient of determination. If there is zero explained variation, i.e., the total variation is all unexplained, this ratio is zero. If there is zero unexplained variation, i.e. the total variation is all explained, the ratio

is one. In other cases the ratio lies between zero and one. Since the ratio is always non-negative, we denote it by  $r^2$ . The quantity  $r$ , called the coefficient of correlation, is given by

$$r = \pm \sqrt{\frac{\text{explained variation}}{\text{total variation}}} = \pm \sqrt{1 - \frac{\sum (\hat{y}_{est} - y)^2}{\sum (y - \bar{y})^2}}$$

and varies between -1 and +1.

If a linear relationship between two variables is assumed, the above equation becomes.

$$r = \frac{\sum (X - \bar{X})(Y - \bar{Y})}{\sqrt{\sum (X - \bar{X})^2 \sum (Y - \bar{Y})^2}}$$

This formula, which automatically gives the proper sign of  $r$ , is called the "product-moment formula" and clearly shows the symmetry between  $X$  and  $Y$ . The above formula can be written in the equivalent form.

$$r = \frac{N \sum XY - (\sum X)(\sum Y)}{\sqrt{N \sum X^2 - (\sum X)^2} \sqrt{N \sum Y^2 - (\sum Y)^2}}$$

In the case of linear correlation the quantity  $r$  is the same regardless of  $X$  or  $Y$ , and it is a very good measure of the linear correlation between two variables.

It must be emphasized that the value of  $r$  computed in any case measures the degree of the relationship relative to the type of equation which is actually assumed. Thus if a linear equation is assumed and the above equation yields a value of  $r$  near zero, it means that there is almost no linear correlation between the variables. However, it does not mean that there is no correlation at all, since there may actually be a high non-linear (e.g. parabolic) correlation between the variables. In other words the correlation coefficient measures the goodness of fit of the equation actually assumed to the data.

It should also be pointed out that a high correlation coefficient (i.e. near 1 or -1) does not necessarily indicate a direct dependence of the variables. Thus, there may be a high correlation between the number of books published each year and the number of hockey games played each year. Such examples are sometimes referred to as "nonsense or spurious correlations" (Ref. 11).

Table 4.1 is an example of the linear correlation coefficients to evaluate the "goodness" of a linear relationship between the TAGA responses at  $m/z = 256$  and at  $m/z = 258$ , both being the two most abundant mass peaks of trichlorobiphenyls. The value 0.992236 indicates that the 256 response and 258 response follow a linear relationship  $Y = 11.625 + 1.00219 X$ . For Column 1 vs Column 3 the TAGA response at  $m/z = 256$  (Y) and equivalent atmospheric concentration (X) follow a linear relationship.

$$Y = 64.6517 + 10.0031X \text{ with } r = 0.975423.$$

Similarly, the TAGA response at  $m/z = 258$  (Y) and equivalent concentration (X) follow a linearity

$$Y = 53.3533 + 9.9267X$$

$$\text{with } r = 0.977681$$

In order to evaluate the feasibility of applying this statistical treatment, a comparison was made between stack gas spiked with PCBs at St. Lawrence Cement and unspiked stack gas. (Table 4.2).

The  $r$  values shown in the left-hand bottom triangle indicate linear correlation coefficients when known amounts of PCBs were added to the stack gas. In contrast the  $r$  values in the other triangle were obtained when no PCB was added to the system. One can see very strong positive linear correlation coefficients (near + 1.0), when PCBs are present in the sample, whereas very weak to negative correlation coefficients were observed when no PCB was present in the sample. Some of these features have been included in our latest computer program PCB MON to facilitate the analysis of PCBs.

#### 4.4 COMPUTER SOFTWARE DEVELOPMENT.

##### 4.4.1 General Outline

The PCB MON Software is a multiple ion monitoring routine designed for the measurement of ambient air for trace amounts of monohexa-chlorobiphenyls. Up to 12 ions may be selected and instrumental parameters may be chosen for each ion separately.

**TABLE 4.1**      **EXAMPLE OF LINEAR CORRELATION COEFFICIENTS**  
**CHARCOAL-FILTERED AMBIENT AIR (March 13, 1980)**

TOTAL RESPONSE VS CONCENTRATION TRICHLOROBIPH			
ROW	1 (256)	2 (258)	3 (ng/m <sup>3</sup> )
1	62 ions	56 ions	0
2	59	47	0
3	77	54	0
4	67	48	0
5	53	42	0
6	65	56	0
7	51	57	0
8	71	51	0
9	285	292	21.51
10	253	260	21.51
11	322	293	21.51
12	285	287	21.51
13	321	292	21.51
14	256	231	21.51
15	255	234	21.51
16	138	131	11.31
17	167	146	11.31
18	195	185	11.31
19	125	95	5.28
20	107	93	5.28
21	91	84	5.28
22	93	89	2.46
23	107	101	2.46
24	82	82	2.46
25	116	92	2.46
26	105	100	2.46

For column 1 versus column 2

Slope	1.00219
Intercept	11.629
Corr. Coef	0.992236

For column 1 versus column 3

Slope	10.0031
Intercept	64.6517
Corr. Coef	0.975423

For column 2 versus column 3

Slope	9.9267	M/Z	3S	Detection Limit
Intercept	53.3533	256	26.4 ions	2.636 ng/m <sup>3</sup>
Corr. Coef	0.977681	258	16.0	1.615

TABLE 4.2 Comparison of r in the presence and absence of PCBs

	222	224	256	258	290	292	324	326	360	362
222		0.755	-0.381	-0.302	-0.597	-0.452	-0.147	-0.115	-0.721	-0.80
224	0.995		0.165	-0.303	-0.435	-0.696	0.365	0.209	-0.203	-0.75
256	0.999	0.995		0.393	0.262	0.232	0.276	0.797	0.551	-0.04
258	0.997	0.996	0.999		0.674	0.614	0.040	0.742	0.377	0.412
290	0.996	0.994	0.997	0.998		0.333	0.311	0.279	0.611	0.698
292	0.995	0.990	0.996	0.995	0.999		-0.660	0.294	-0.065	0.254
324	0.991	0.987	0.994	0.993	0.997	0.999		0.265	0.759	0.319
326	0.990	0.985	0.993	0.992	0.997	0.999	1.000		0.443	-0.01
360	0.994	0.989	0.995	0.994	0.998	0.999	0.999	0.999		0.698
362	0.991	0.986	0.993	0.992	0.997	0.999	0.999	0.999	0.999	



The software also provides isotope ratio calculations and statistics, which permit the operator to place a degree of confidence in the measurements. Additionally, the software will control the automated short term integrator sampling and measurement sequences. After sample collection from a known volume of air, the wire coil is resistively heated to desorb or elute the PCBs for ionization and detection with TAGA<sup>TM</sup> systems.

#### 4.4.2. Sample Output

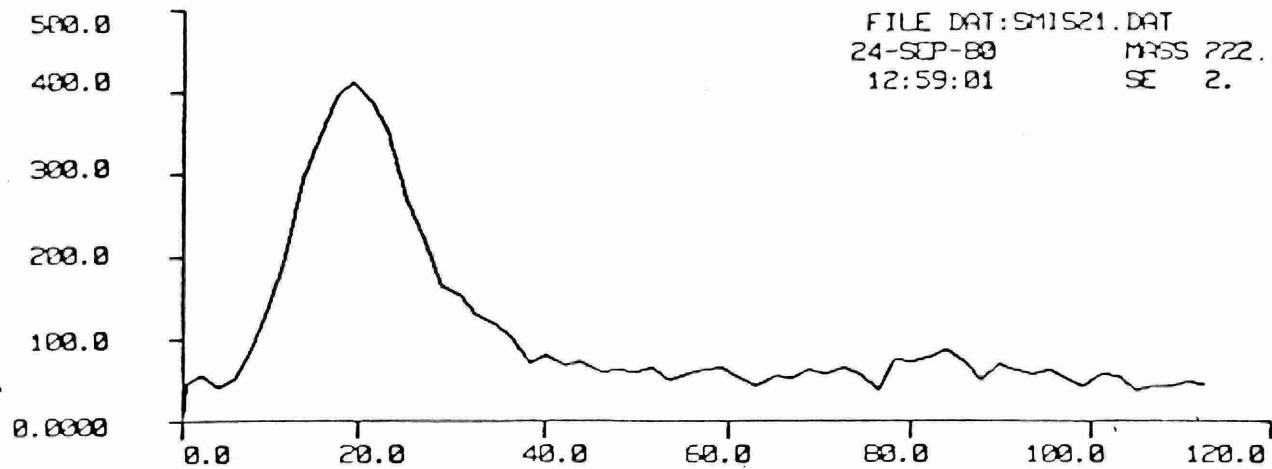
A sample desorption curve (ion counts vs. time) is shown in Figure 4.2 with a measurement report indicating in columns from left to right:

- (i) m/z of the ion of interest;
- (ii) integrated ion counts between adjustable start (ST) and end (EN) times;
- (iii) theoretical ion ratios (M2/M1, M4/M3, M6/M5, etc.);
- (iv) observed integrated ion count ratios.

Useful indexing and filing information are displayed in the upper right hand corner of the plot, indicating date, time of day, file name, sequence number and displayed mass. The desorption plot can be obtained for any mass for selection of integration limit.

#### 4.4.3. Parameter Table

In the sample parameter table shown in Figure 4.3, the operator can select different instrumental parameters for each ion of interest. By selecting the appropriate mass index number (M1) in the far left hand column, the operator can revise ion lens potentials (L1-L5)\*, rod offset (RO)\*, resolution (RE), m/z (MS), sampling time (T1), theoretical ion ratio (RA), or start (ST) and end (EN) of signal integration time.



MASS	IONS	CONC	THERRAT	OBRRAT
78	2097.		0.00	0.45
188	944.			
222	4232.		0.65	0.80
224	3403.			
256	36592.		0.98	0.96
258	35180.			
290	2688.		1.30	1.29
292	3456.			
323	4291.		1.63	1.47
325	6312.			
359	683.		0.81	0.84
361	573.			

MONITORING ON SITE #3 NEAR WESTERN FENCELINE

Figure 4.2 Measurement Report - PCB Monitoring

ONE										
19-AUG-78						MO 0.00000		MI 1.0000		
SY 0.		AS 00:00:00		DS 60.000		WS -5.1200		MU -4500.0		
SE 0.		AT 120.00		DF 47.000		WD -5.1200		DI 3.0000		
OP 0.		AF 4.5000		PR 0.00000		OT -5.1200		IN 700.00		
1	MS	77.00	RE	125.0	R0	16.00	TI	3.000	RA 0.0000	ST 35.00
	L1	46.00	L2	22.00	L3	9.000	L4	-250.0	L5 -5.000	EN 40.00
2	MS	187.6	RE	135.0	R0	20.00	TI	9.000	RA 0.0000	ST 8.000
	L1	46.00	L2	21.00	L3	8.000	L4	-250.0	L5 -5.000	EN 45.00
3	MS	221.5	RE	135.0	R0	22.00	TI	9.000	RA 0.6500	ST 10.00
	L1	46.00	L2	22.00	L3	8.000	L4	-250.0	L5 0.0000	EN 54.00
4	MS	223.5	RE	135.0	R0	22.00	TI	9.000	RA 0.6500	ST 10.00
	L1	46.00	L2	22.00	L3	8.000	L4	-250.0	L5 0.0000	EN 54.00
5	MS	255.5	RE	128.0	R0	18.00	TI	9.000	RA 0.9750	ST 9.000
	L1	43.00	L2	22.00	L3	7.000	L4	-250.0	L5 0.0000	EN 57.00
6	MS	257.5	RE	128.0	R0	18.00	TI	9.000	RA 0.9750	ST 9.000
	L1	43.00	L2	22.00	L3	7.000	L4	-250.0	L5 0.0000	EN 57.00
7	MS	289.5	RE	128.0	R0	23.00	TI	9.000	RA 1.300	ST 8.000
	L1	45.00	L2	21.00	L3	7.000	L4	-250.0	L5 0.0000	EN 53.00
8	MS	291.5	RE	128.0	R0	23.00	TI	9.000	RA 1.300	ST 8.000
	L1	45.00	L2	21.00	L3	7.000	L4	-250.0	L5 0.0000	EN 53.00
9	MS	323.4	RE	122.0	R0	20.00	TI	9.000	RA 1.630	ST 9.000
	L1	45.00	L2	22.00	L3	8.000	L4	-250.0	L5 0.0000	EN 49.00
10	MS	325.4	RE	122.0	R0	20.00	TI	9.000	RA 1.630	ST 9.000
	L1	45.00	L2	22.00	L3	8.000	L4	-250.0	L5 0.0000	EN 49.00
11	MS	359.4	RE	122.0	R0	23.00	TI	9.000	RA 0.8120	ST 10.00
	L1	46.00	L2	22.00	L3	9.000	L4	-250.0	L5 -5.000	EN 49.00
12	MS	361.4	RE	122.0	R0	23.00	TI	9.000	RA 0.8120	ST 10.00
	L1	46.00	L2	22.00	L3	9.000	L4	-250.0	L5 -5.000	EN 49.00

Figure 4.3 Parameter Table - PCB Monitoring

Other pertinent parameters above the main table include:

<u>Parameter</u>	<u>Description</u>
MU	multiplier voltage
DI	discharge current
IN	interface plate voltage
AS	time of day
AT	adsorption time
SY	system number
SE	sequence number
OP	operator number
AF	air flow
OT	outside temperature
WS	wind speed
WD	wind direction
DT	desorption time
DF	desorption flow
PR	probe parameter

#### 4.4.4 Summarized Data Report

A sample summarized data report is shown in Figure 4.4. This report presents statistical information on a selected series of measurements, in this case 8 (N=8) measurements of the background ambient air at a calibration site. MASS, THERAT and OBSRAT are as described in Section 4.4.2. The AVION is the mean of the integrated ion counts for the 8 observations at each of the background subtractions for subsequent readings relative to this calibration site and to calculate time weighted average concentrations from measurements on a site of interest. The standard deviations of the AVIONS, i.e., in the S column however, are only of interest as a measure of reproducibility of background measurements and calibration points.

The R column refers to the correlation between the chlorine isotope peaks (M1 & M2, M3 & M4, M5 & M6, etc.), for each degree of chlorination.

MASS	IONS	CONC	THERAT	OSRAT	AVION	S	R
78			0.00	0.02	18458.	92.	0.352
188					297.	19.	
222			0.65	1.34	237.	22.	0.137
224					319.	14.	
256			0.98	0.86	1580.	100.	0.957
258					1363.	83.	
290			1.30	1.18	64.	7.	0.617
292					75.	8.	
323			1.63	1.36	355.	24.	0.154
325					484.	31.	
359			0.81	0.78	78.	9.	0.291
361					61.	8.	

BACKGROUND BEFORE INJECTIONS SITE #1

N= 8

Figure 4.4 Summarized Data Report - PCB Monitoring

This is essentially a measure of whether the isotope peaks fluctuate together. This is designed to aid the operator in placing a degree of confidence in the measurements, since as R approaches 1, it is increasingly likely that the 2 ions of interest originate from the same compound.

## 5. PRELIMINARY TESTING FOR MONITORING CAPABILITY (AMBIENT AIR)

During Phase I and toward the end of Phase III the MOE TAGA<sup>TM</sup>3000 unit was dedicated to the preliminary testing for ambient air PCB monitoring capability.

### 5.1 System Response

Outdoor air was drawn through 22 mm O.D., 19mm I.D. glass tubes into the PCB wire integrator for sample collection at 50°C. After collecting a number of background readings, known amounts of PCBs were added to the sampling line using a heated glass injection port (See Fig. 3.17). The data acquisition was made by the PCBMON program, and the data reduction was done by the PCBGEN program.

As an example of the system response, outdoor air was taken at the St. Lawrence Cement premises in Mississauga, Ontario, and it was filtered through 1.8 kg activated charcoal, 6-14, mesh before introducing into the TAGA system. Tables 5.1, 5.2, 5.3, 5.4, 5.5, and 5.6 indicate the system responses in ions, equivalent atmospheric PCB concentrations in ng/m<sup>3</sup>, sensitivities (= slope), intercepts and linear correlation coefficients. At the bottom of each Table the values show three (3) times standard deviations of the background readings when no PCB was added to the system. Detection limits in ng/m<sup>3</sup> were calculated by dividing the 3s with the corresponding sensitivity.

Figures 5.1, 5.2, 5.3, 5.4, 5.5 and 5.6 are graphic presentations of these results. Table 5.7 summarizes these detection limits, linear correlation coefficients, sensitivities, calculated and observed isotopic abundance ratios, and percent deviation between the observed and calculated isotopic abundance ratios.

TABLE 5.1 CHARCOAL-FILTERED AMBIENT AIR (March 13, 1980)

TOTAL RESPONSE VS CONCENTRATION MONOCHLOROBIPHENYL

ROW	1 (188)	2 (ng/m <sup>3</sup> )
1	129 ions	0
2	123	0
3	127	0
4	148	0
5	130	0
6	119	0
7	144	0
8	123	0
9	355	22.51
10	361	22.51
11	434	22.51
12	428	22.51
13	369	22.51
14	360	22.51
16	255	11.81
17	293	11.81
18	265	11.81
19	228	5.53
20	193	5.53
21	246	5.53
22	200	2.57
23	204	2.57
24	249	2.57
25	228	2.57
26	219	2.57

For column 1 versus column 2

Slope 9.77347  
 Intercept 155.653  
 Corr. Coef 0.931091

M/Z 3s Detection Limit  
 188 31.0 ions 3.173 ng/m<sup>3</sup>

TABLE 5.2

CHARCOAL-FILTERED AMBIENT AIR (March 13, 1980)

TOTAL RESPONSE VS CONCENTRATION DICHLOROBIPHENYL

ROW	1 (222)	2 (224)	3 (ng/m <sup>3</sup> )
1	205 ions	177 ions	0
2	164	182	0
3	218	190	0
4	175	188	0
5	179	193	0
6	185	181	0
7	208	171	0
8	178	179	0
9	476	337	15.25
10	453	346	15.25
11	509	418	15.25
12	466	399	15.25
13	480	372	15.25
14	426	364	15.25
15	438	312	15.25
16	320	281	8.02
17	326	250	8.02
18	309	293	8.02
19	282	244	3.74
20	256	238	3.74
21	259	236	3.74
22	227	234	1.74
23	243	237	1.74
24	218	207	1.74
25	252	224	1.74
26	219	200	1.74

For column 1 versus column 2

Slope 1.45126  
 Intercept 76.3156  
 Corr. Coef 0.967365

For column 1 versus column 3

Slope 17.6438  
 Intercept 192.752  
 Corr. Coef 0.98304

For column 2 versus column 3

Slope 11.451  
 Intercept 189.5  
 Corr. Coef 0.958375

M/Z	3S	Detection Limit
222	56.9 ions	3.224 ng/m <sup>3</sup>
224	21.9	1.914



TABLE 5.3 CHARCOAL-FILTERED AMBIENT AIR (March 13, 1980)

TOTAL RESPONSE VS CONCENTRATION TRICHLOROBIPHENYL

ROW	1 (256)	2 (258)	3 (ng/m <sup>3</sup> )
1	62 ions	56 ions	0
2	59	47	0
3	77	54	0
4	67	48	0
5	53	42	0
6	65	56	0
7	51	57	0
8	71	51	0
9	285	292	21.51
10	253	260	21.51
11	322	293	21.51
12	285	287	21.51
13	321	292	21.51
14	256	231	21.51
15	255	234	21.51
16	138	131	11.31
17	167	146	11.31
18	195	185	11.31
19	125	95	5.28
20	107	93	5.28
21	91	84	5.28
22	93	89	2.46
23	107	101	2.46
24	82	82	2.46
25	116	92	2.46
26	105	100	2.46

For column 1 versus column 2

Slope 1.00219  
Intercept 11.629  
Corr. Coef 0.992236

For column 1 versus column 3

Slope 10.0031  
Intercept 64.6517  
Corr. Coef 0.975423

For column 2 versus column 3

Slope 9.9267  
Intercept 53.3533  
Corr. Coef 0.977681

M/Z	3s	Detection Limit
256	26.4 ions	3.224 ng/m <sup>3</sup>
258	16.0	1.615

TABLE 5.4 CHARCOAL-FILTERED AMBIENT AIR (March 13, 1980)

TOTAL RESPONSE VS CONC TETRACHLOROBIPHENYL

<u>ROW</u>	<u>1 (290)</u>	<u>2 (292)</u>	<u>3 (ng/m<sup>3</sup>)</u>
1	38	32	0
2	40	50	0
3	29	34	0
4	30	27	0
5	45	28	0
6	30	43	0
7	35	35	0
8	50	48	0
9	248	301	27.82
10	255	304	27.82
11	284	357	27.82
12	263	329	27.82
13	293	341	27.82
14	246	300	27.82
15	225	296	27.82
16	148	167	14.63
17	164	203	14.63
18	160	228	14.63
19	83	109	6.83
20	79	108	6.83
21	81	109	6.83
22	66	94	3.18
23	80	95	3.18
24	68	76	3.18
25	95	95	3.18
26	93	86	3.18

For column 1 versus column 2

Slope 0.78572  
 Intercept 41.323  
 Corr. Coef 0.992665

For column 1 versus column 3

Slope 7.83072  
 Intercept 41.323  
 Corr. Coef 0.985036

For column 2 versus column 3

Slope 9.92946  
 Intercept 44.7771  
 Corr. Coef 0.988343

M/Z	3s	Detection Limit
290	22.9 ions	2.928 ng/m <sup>3</sup>
292	26.5	2.666

TABLE 5.5 CHARCOAL-FILTERED AMBIENT AIR (March 13, 1980)

TOTAL RESPONSE VS CONC PENTACHLOROBIPHENYL			
ROW	1 (324)	2 (326)	3 (ng/m <sup>3</sup> )
1	39 ions	79 ions	0
2	34	64	0
3	41	67	0
4	40	80	0
5	35	67	0
6	40	75	0
7	40	67	0
8	39	72	0
9	165	267	23.25
10	146	286	23.25
11	204	319	23.25
12	183	294	23.25
13	184	325	23.25
14	161	256	23.25
15	141	238	23.25
16	108	158	12.23
17	112	196	12.23
18	129	188	12.23
19	74	114	5.71
20	87	120	5.71
21	56	105	5.71
22	65	118	2.66
23	83	125	2.66
24	41	86	2.66
25	72	110	2.66
26	69	97	2.66

For column 1 versus column 2

Slope 0.607285  
 Intercept 0.951724  
 Corr. Coef 0.938951

For column 1 versus column 3

Slope 5.48545  
 Intercept 43.3485  
 Corr. Coef 0.963421

For column 2 versus column 3

Slope 9.00585  
 Intercept 73.1855  
 Corr. Coef 0.976222

M/Z	3s	Detection Limit
324	7.7 ions	1.402 ng/m <sup>3</sup>
326	18.2	2.022

TABLE 5.6 CHARCOAL-FILTERED AMBIENT AIR (March 13, 1980)

TOTAL RESPONSE VS CONCENTRATION HEXACHLOROBIPHENYL

ROW	1 (360)	2 (362)	3 (ng/m <sup>3</sup> )
1	32 ions	19 ions	0
2	26	18	0
3	18	30	0
4	32	28	0
5	26	19	0
6	37	20	0
7	31	26	0
8	25	26	0
9	214	196	52.23
10	236	229	52.23
11	258	249	52.23
12	220	227	52.23
13	229	204	52.23
14	196	187	52.23
15	168	164	52.23
16	114	90	27.46
17	131	128	27.46
18	129	120	27.46
19	64	57	12.81
20	60	60	12.81
21	70	49	12.81
22	65	51	5.97
23	73	64	5.97
24	42	38	5.97
25	85	72	5.97
26	73	56	5.97

For column 1 versus column 2

Slope 1.00754  
 Intercept 8.02664  
 Corr. Coef 0.99384

For column 1 versus column 3

Slope 3.5251  
 Intercept 32.0807  
 Corr. Coef 0.973035

For column 2 versus column 3

Slope 3.47627  
 Intercept 24.3194  
 Corr. Coef 0.972789

M/Z	3s	Detection Limit
360	17.5 ions	4.961 ng/m <sup>3</sup>
362	14.2	4.743

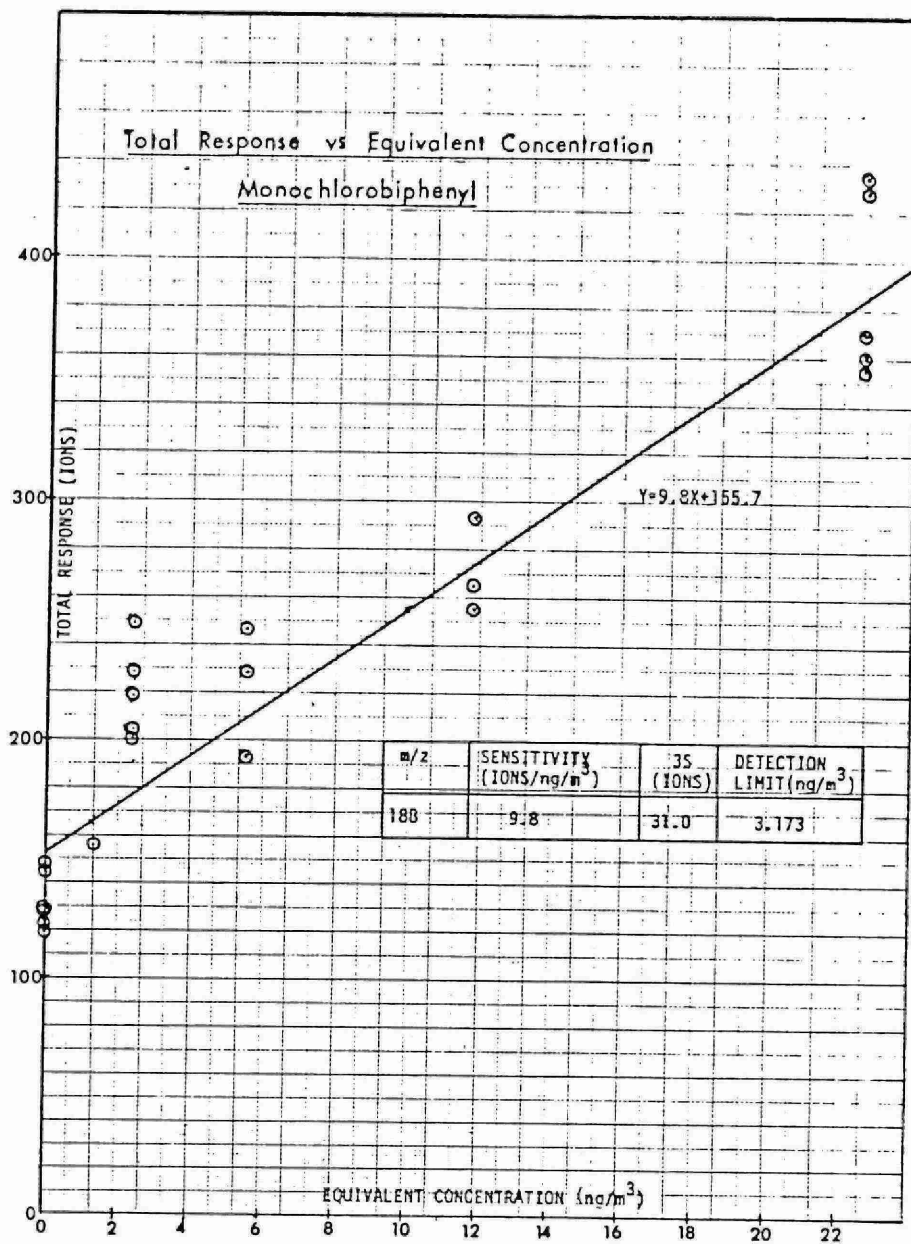


Figure 5.1

# Total Response vs Equivalent Concentration

## Dichlorobiphenyl

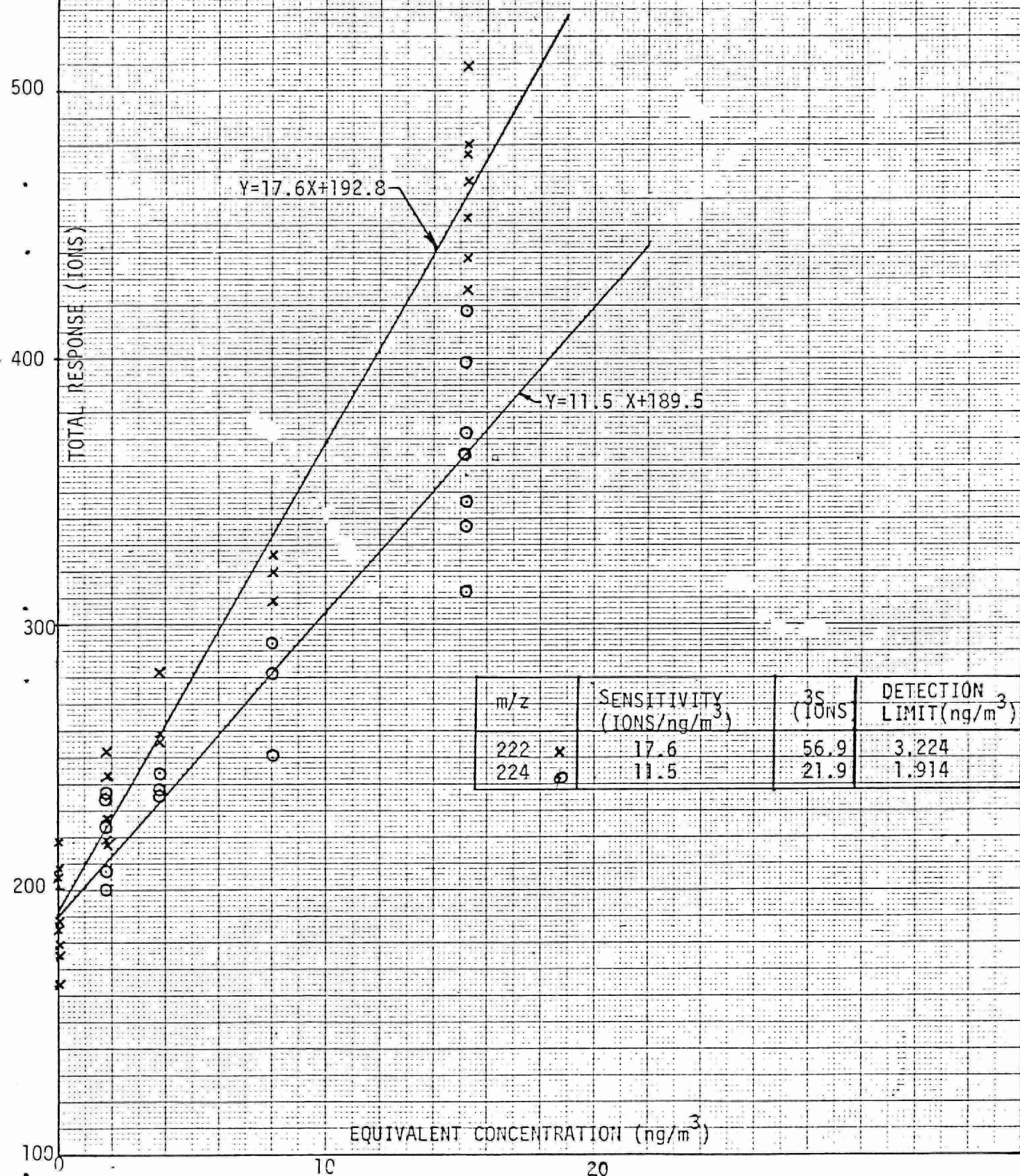


Figure 5.2

7550549



# Total Response vs Equivalent Concentration

## Trichlorobiphenyl

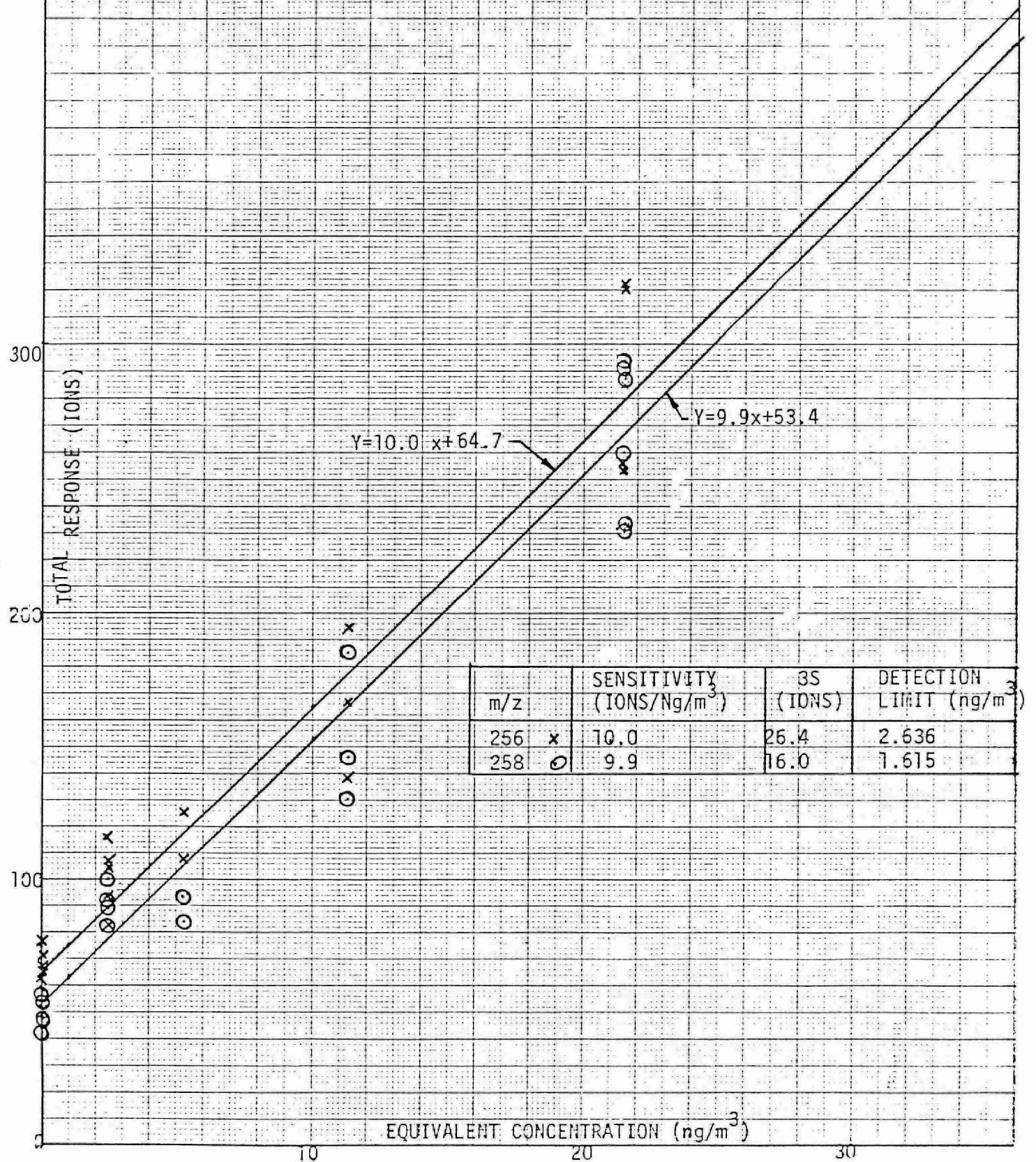


Figure 5.3

# Total Response vs Equivalent Concentration

## Tetrachlorobiphenyl

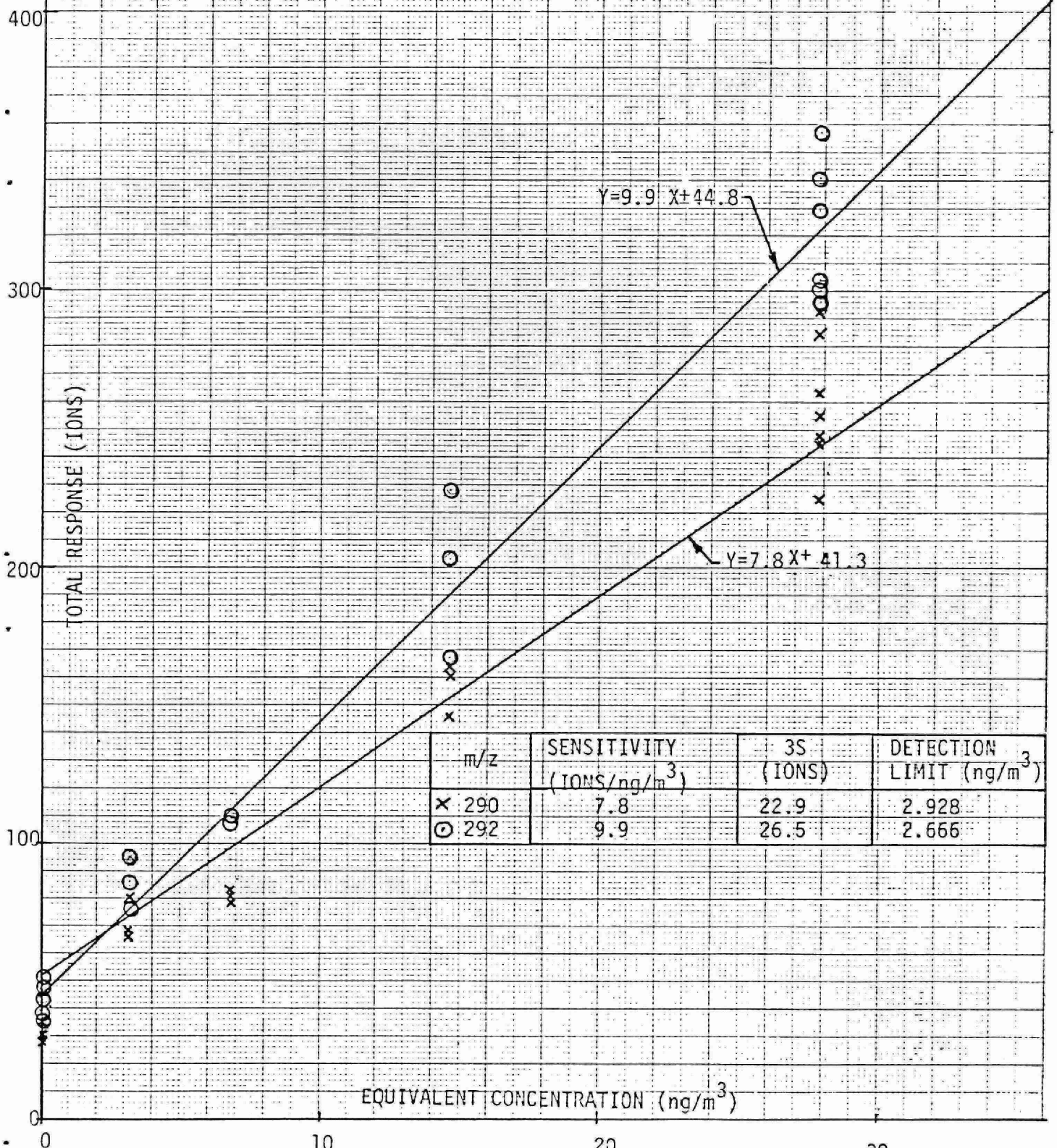


Figure 5.4



# Total Response vs Equivalent Concentration

## Pentachlorobiphenyl

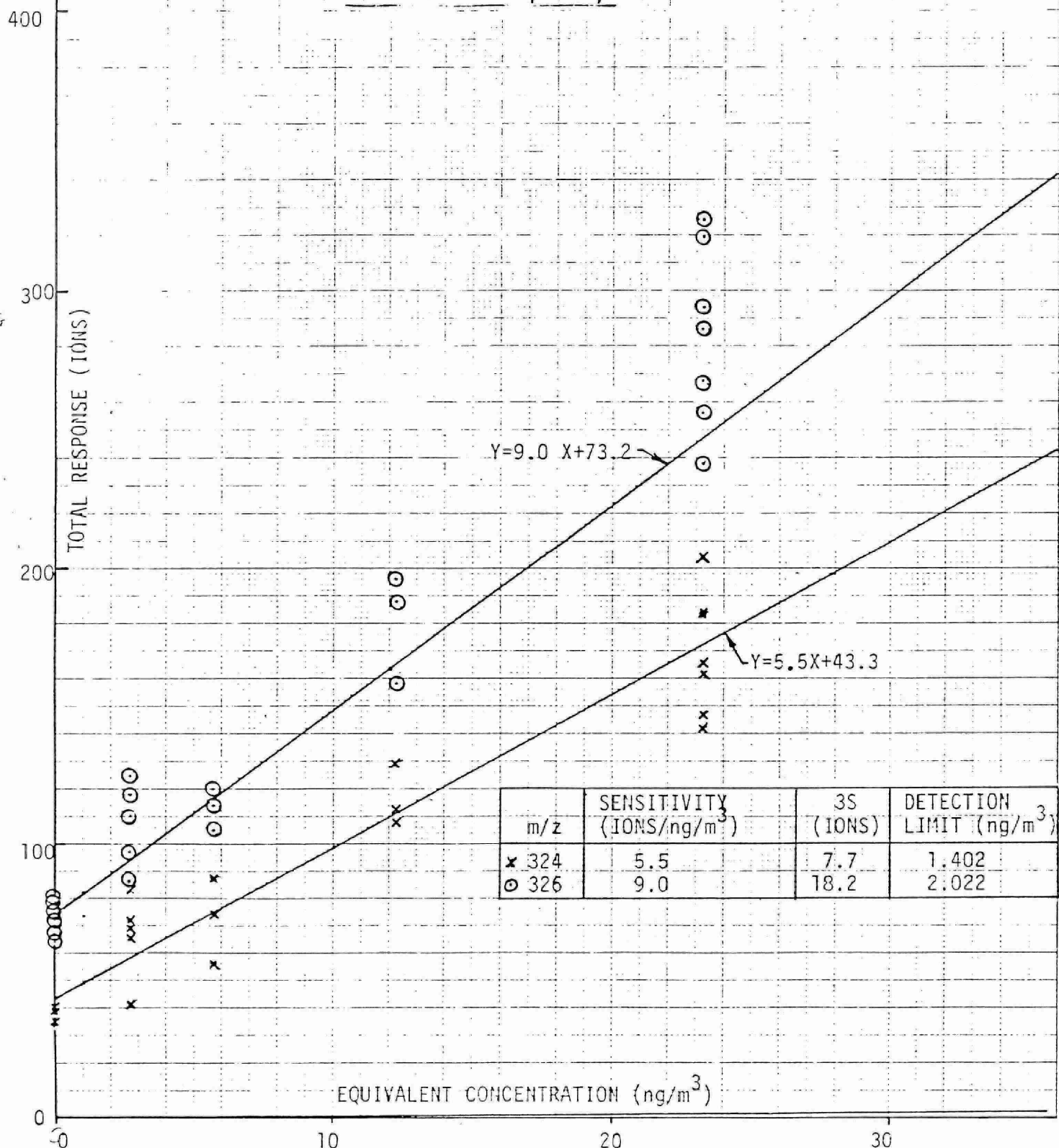


Figure 5.5

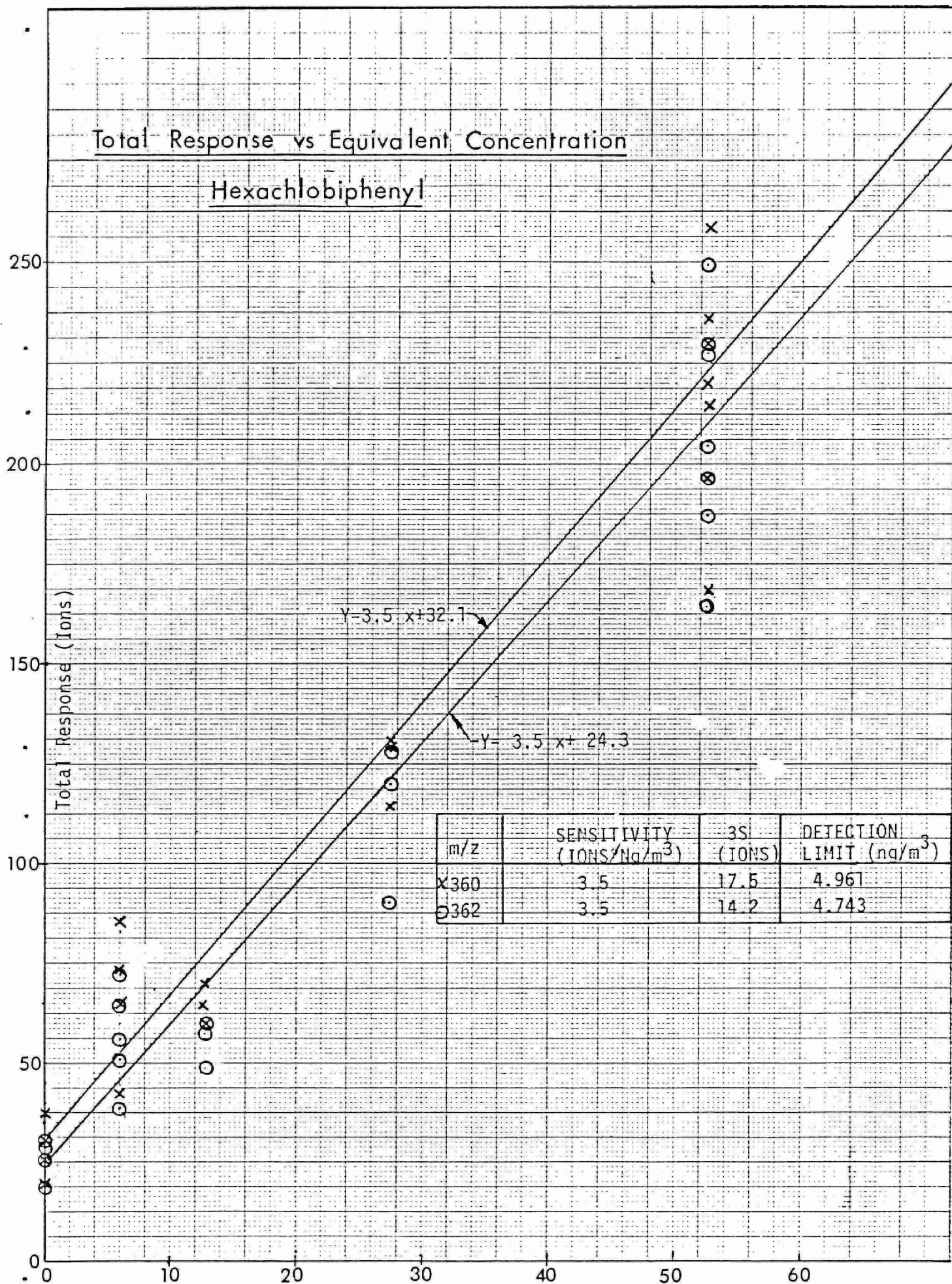


Figure 5.6

TABLE 5.7

## SUMMARY OF RESULTS

RESPONSE VS PCB CONCENTRATION: CHARCOAL-FILTERED AMBIENT AIR

PCB SPECIES	MONO	DI		TRI		TETRA		PENTA		HEXA	
M/Z	188	222	224	256	258	290	292	324	326	360	362
Detection Limit (ng/m <sup>3</sup> )	3.173	3.224	1.914	2.636	1.165	2.929	2.666	1.402	2.022	4.961	4.743
Sensitivity (slope) (ions/ng/m <sup>3</sup> )	9.773	17.644	11.451	10.003	9.927	7.831	9.929	5.485	9.006	3.525	3.476
Observed Isotopic Abundance ratio (%)			64.9	99.2		78.9		60.9		98.6	
Theoretical Isotopic Abundance ratio (%)			65.0	97.5		76.9		61.5		81.2	
% Deviation between obs. & theor. ratios			0.2	1.7		2.6		1.0		21.4	
Corr Coef (response vs Conc.)	0.931	0.984	0.958	0.975	0.978	0.985	0.988	0.963	0.976	0.973	0.973
Corr Coef (between isomers)			0.967	0.992		0.993		0.984	0.994		

As shown in Table 5.7 the "worst case" minimum detectability, i.e. sum of best detection limits for mono to hexachlorobiphenyl, is 15.513 ng/m<sup>3</sup>. Except for the hexachlorobiphenyl the observed isotopic abundance ratios and calculated abundance ratios agree well (within 3%). The large deviation observed for the hexachlorobiphenyl species (21.4%) may arise from the relatively high background fluctuation, and the relatively poor sensitivity at the m/z of interest.

The high detection limits for the hexachlorobiphenyl is attributed to several factors:

- (1) Transmission of the mass filter decreases as the mass increases.
- (2) The higher PCBs are composed of more isotopic species so that the same number of ions are distributed into more channels (m/z).
- (3) An increase in ionization potential of the higher chlorinated biphenyls resulting in slower charge exchange reaction rates with the benzene reagent ions.
- (4) The presence of a high background fluctuation in the hexachlorobiphenyl region due to an unknown (locally strong) chemical contaminant caused an increase in the chemical noise, at the particular time and location.

The first three factors cause an approximate loss of a factor of 2-5 in sensitivity which affects the detection limit by decreasing the available ion signal. A few suggestions to improve the detection limits will be made in the final chapter.

## 5.2 TAGA Response to Various Isomers

A brief study was undertaken to determine the relative response of the MOE TAGA<sup>TM</sup> 3000 unit to several PCB isomers. A total of 64 PCB solutions were prepared by the Ministry. Because of the shift of project priorities assigned to the van, all the standards were not evaluated. This study was undertaken in the early stage of Phase I, and the introduction of these solutions was made with the prototype GLC injector (See Figure 3.22C) or with a tungsten loop (Fig. 3.22b). The accuracy of these results

was therefore not so good as those obtained at the end of this whole project. The accuracy lay  $\pm 20 - \pm 30\%$ . Nevertheless, Table 5.8, which compares isomeric responses shows a general trend, i.e., isomers possessing chlorine atom(s) in the ortho region are not so sensitive as meta-or para-substituted biphenyls. This appears to be a very interesting topic, and a further study may elucidate the relationship between the ionization potential of PCBs and their isomeric position.

Hexachlorobiphenyls were not measured because of the serious interference problems experienced at the time of the analysis. Since then, the analytical technology has improved significantly, and a more detailed study is possible to elaborate this kind of isomeric comparison.

TABLE 5.8

COMPARISON OF ISOMERIC RESPONSES

<u>Compounds</u>		
<u>MONOCHLOROBIPHENYLS</u>	<u>m/z</u>	<u>Sensitivity (ions)</u> ng
2-	188	27
	190	26
3-	188	118
	190	40
4-	180	110
	190	75
<u>DICHLOROBIPHENYLS</u>		
2,3-	222	351
	224	200
2,4-	222	301
	224	205
2,5-	222	224
	224	165
<u>TRICHLOROBIPHENYLS</u>		
2,2,5-	256	70
	258	58
2,3,4-	256	242
	258	239
2,3,5-	256	226
	258	298

TABLE 5.8 (Continued)

<u>TETRACHLOROBIPHENYLS</u>	<u>m/z</u>	<u>Sensitivity (ions)</u> ng
2,2 ,6,6 -	290	47
	292	73
2,2 ,5,6-	290	89
	292	191
2,2 ,3 ,5-	290	175
	292	237
<hr/>		
<u>PENTACHLOROBIPHENYS</u>		
2,3,4,5,6-	324	100
	326	163
2,2 ,3,4,6-	324	42
	326	74
2,3 ,4,4 ,6-	324	122
	326	206
<hr/>		

### 5.3 Filtration of Ambient Air

In order to obtain stable background readings for PCB calibration, attempts were made to secure a clean air source in Phase I and towards the end of Phase III. A cylinder of prepurified air, activated charcoal and Florisil were evaluated, and compared.

#### 5.3.1. Prepurified Air Cylinder

Size 1A gas cylinder contains  $6.23 \text{ m}^3$  of purified air at 760 mmHg at  $21^\circ\text{C}$ . In theory one can use one cylinderfull of air for 52 minutes at 2 l/s of flow rate. However, our experiment indicates that one cylinder can be used for only 30 minutes or so, and severe temperature drop was experienced due to the rapid gas expansion, say, from 149.6 atm (2200 psi) to 1 atmospheric pressure (14.7 psi). It is very difficult to heat up this cold air without contaminating the gas. For these reasons this option was not pursued further.

#### 5.3.2. Florisil Trap

Florisil, 60-100 mesh, is a highly selective adsorbent which has found extensive use in preparative and analytical chromatography. It is a magnesia-silica gel manufactured by Floridian Company, Three Penn Centre, Pittsburgh, PA, and was purchased from Fisher Scientific Co., Toronto, Ontario.

The material, weighing approximately 500g, was placed in a large porcelain dish, and heated at  $400^\circ\text{C}$  for 12 hours in a gentle stream of nitrogen to flush any organic matter permeating from the adsorbent out of the muffle furnace.

After cooling, the baked Florisil was placed in the custom-made funnel shown in Figure 5.7. Outdoor air in an agricultural area was drawn at 2 l/s, and a number of readings were made using a PCB wire integrator and DSORBA program. The trapping efficiencies of Florisil at several m/z values are shown in Table 5.9. These values were obtained by dividing the response difference between unfiltered and filtered air by the response of unfiltered air, followed by a multiplication with 100.



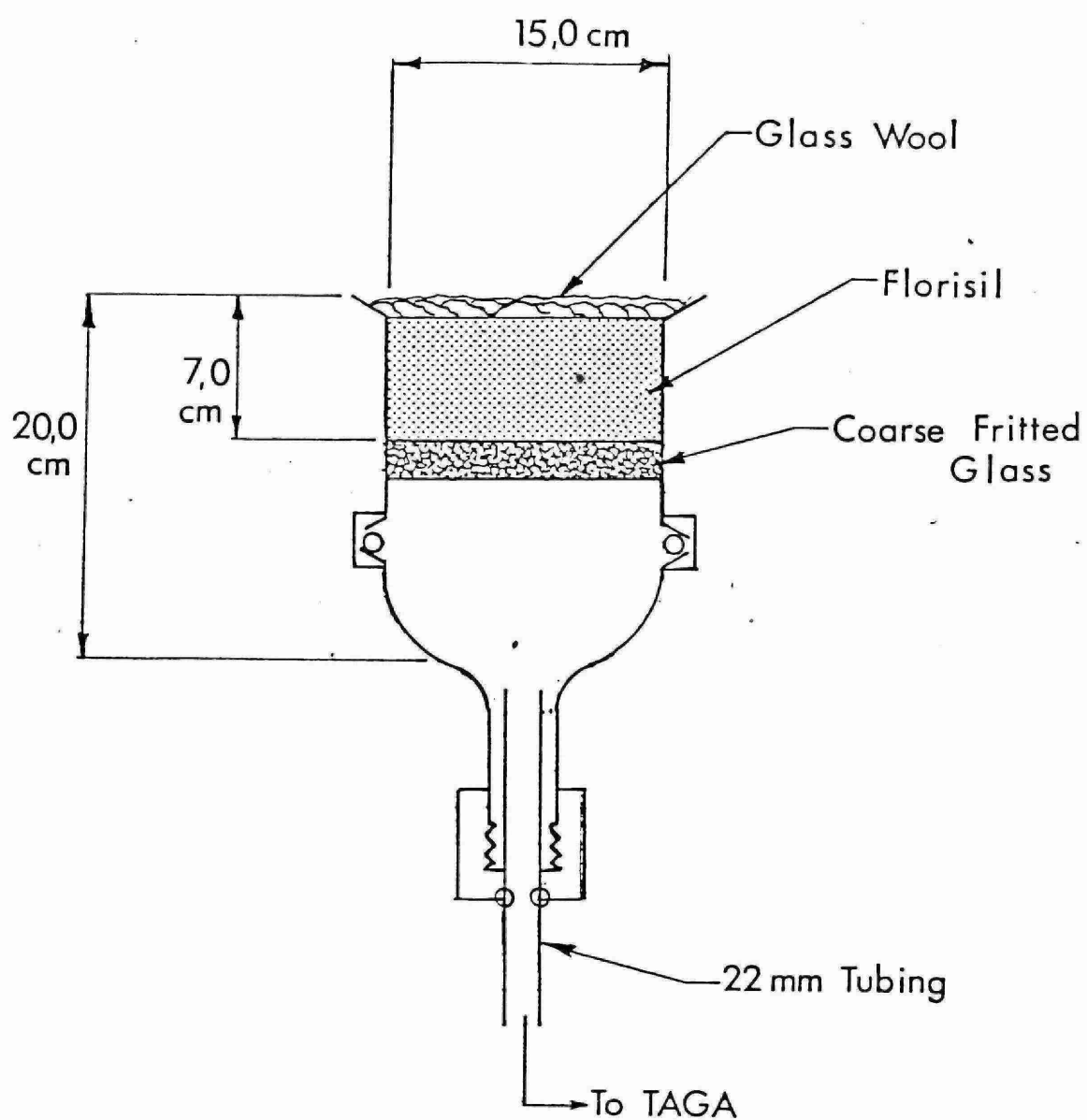


Figure 5.7  
SCHEMATIC of a CUSTOM MADE FUNNEL

TABLE 5.9

TRAPPING EFFICIENCY OF FLORISIL

m/z	NO FILTRATION			FILTRATION			EFFICIENCY <sup>*</sup>
	n <sub>1</sub>	x <sub>1</sub>	s <sub>1</sub>	n <sub>2</sub>	x <sub>2</sub>	s <sub>2</sub>	
188	7	3741	712.8	3	3052	141.2	18.4+12.7%
190	7	3714	603.3	3	2860	188.8	23.0+11.7%
222	7	4472	461.0	3	2804	187.5	37.3+7.5%
224	7	4172	547.5	3	2896	267.3	30.6+9.7%
324	7	1631	182.2	5	554	78.9	66.0+7.0%
326	7	2402	382.8	4	433	35.8	82.0+10.0%
360	6	732	160.7	4	160	13.3	78.1+13.5%
362	6	666	91.0	4	101	46.9	84.8+9.1%

The percent errors were calculated by dividing the root square of the pooled variance with the response of the unfiltered air, followed by multiplication with 100. Results were not obtained for trichlorobiphenyl and tetrachlorobiphenyl vegious, because at the time of this experiment the DSORBA could only monitor only eight (8) ion species in the fast peak jumping mode.

Table 5.9 indicates that the pre-conditioned Florisil adsorb interfering chemicals in the higher PCB regions, but not in the light PCB regions.

### 5.3.3 Activated Charcoal

#### 5.3.3.1 MSA Chemical Cartridge GMA Organic Vapors.

A circular chemical cartridge, 80 mm diameter x 25 mm thick, Part No. 459315 made by Mine Safety Appliance Co., Pittsburgh, PA., USA 15208, was attached to the top of the TAGA<sup>TM</sup> sample line, using a custom made Pyrex reducer (22 mm to 80 mm). The edge of the cartridge was sealed with a commercial Teflon tape to prevent any leak. Readings were made before and after the installation of this cartridge. No significant signal change was observed. It was concluded that the cartridge was not suited to treat a large volume of air at the relatively high flow rate of 2 l/sec.

#### 5.3.3.2 Coconut charcoal.

Activated coconut charcoal, 6-14 mesh, 1-8 kg in a steel can, 17 cm diameter x 21 cm high, was purchased from Fisher Scientific (5-685B), Toronto, Ontario. The charcoal was temporarily stored in a clean container. The empty can was then modified to accommodate 2 pieces of 10 cm x 19 mm I.D. copper tubes at the top and bottom, so that air can flow through the can (Figure 5.8). A wad of clean glass wool was placed at the bottom, then the charcoal was put back. A wad of glasswool was placed at the top of the charcoal before placing the top. A duplicate filter was made to examine the amount and contact time of activated coconut charcoal with the sample air.

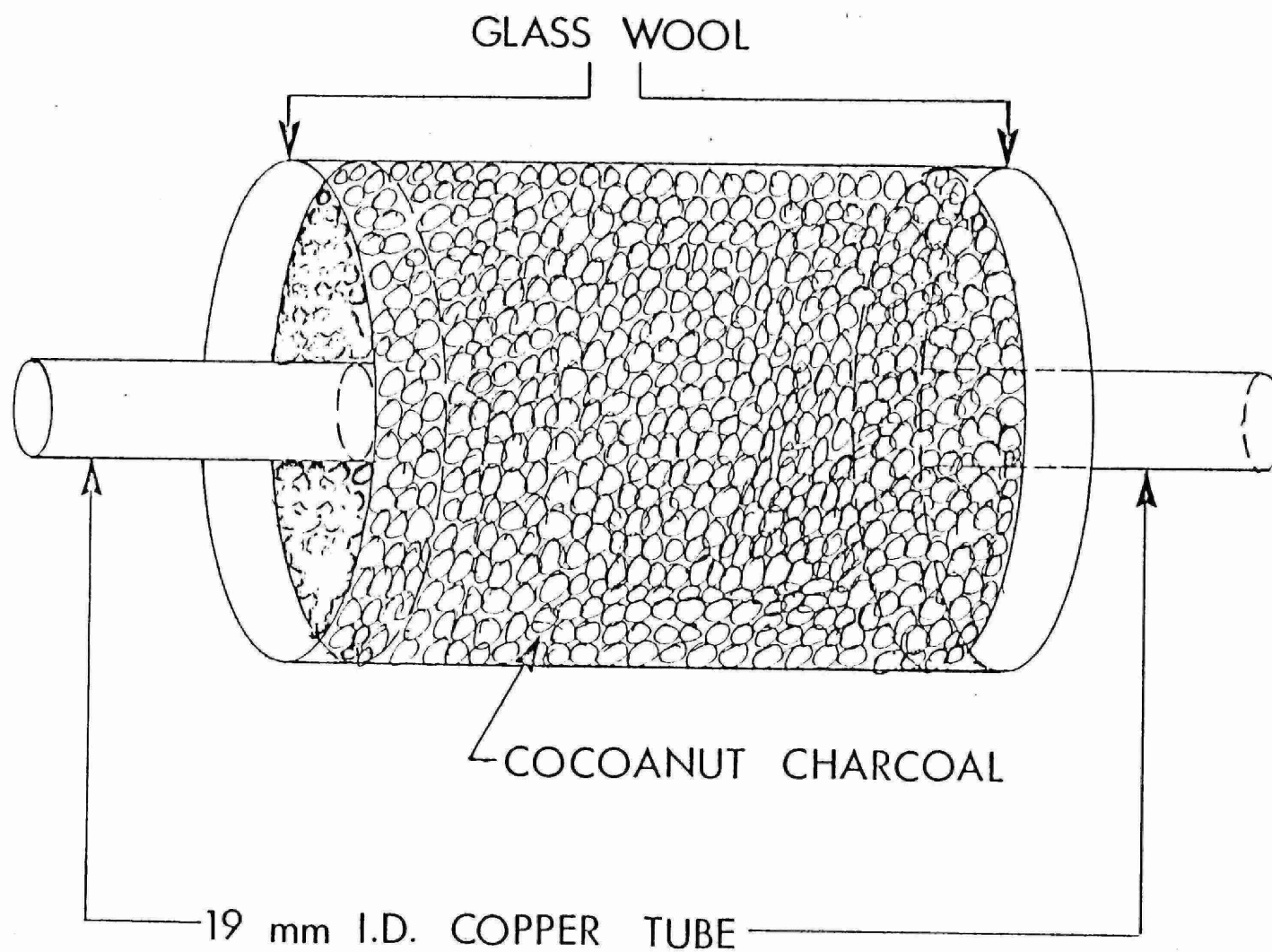


Figure 5.8 CHARCOAL FILTER

This experiment was undertaken at the St. Lawrence Cement sampling point by sampling outdoor air. At the beginning of this experiment the MOE TAGA<sup>TM</sup> 3000 system was operated with the high peak resolving power, i.e., high resolution valve. When a comparison was made between the unfiltered outdoor air and the filtered air under this high resolving condition, the difference was insignificant due to the lack of sensitivity. In order to enhance the difference, the TAGA resolution was dropped to allow more signal to reach the ion detection system.

At first, a number of readings were made by drawing outdoor air directly into the wire integrator region. Then, a filter was placed in line to collect several stable readings. After this, an additional filter was placed in series to obtain some more readings. These results are tabulated in Table 5.10. The results shown in this table indicate that:

- (1) the charcoal is a poor adsorbent when compared with results shown in Table 5.9 for Florisil, especially in the high mass region. However, this charcoal traps low mass species better than Florisil.
- (2) doubling the charcoal trap does not increase its trapping efficiency.

TABLE 5.10

TRAPPING EFFICIENCY OF COCONUT CHARCOAL

m/z	Double Filter			Single Filter		No Filter					
	n <sub>1</sub>	x <sub>1</sub>	s <sub>1</sub>	e <sub>1</sub> (%)	n <sub>2</sub>	x <sub>2</sub>	s <sub>2</sub>	e <sub>2</sub> (%)	n <sub>3</sub>	x <sub>3</sub>	s <sub>3</sub>
188	3	309	7	49.5 <sub>+4.8</sub>	4	322	15	46.6 <sub>+4.5</sub>	3	612	4
222	3	1177	63	34.3 <sub>+2.8</sub>	4	1225	23	31.7 <sub>+1.2</sub>	3	1794	5
224	3	1445	97	14.0 <sub>+4.0</sub>	4	1375	33	18.2 <sub>+2.1</sub>	3	1681	5
256	3	622	12	13.5 <sub>+1.3</sub>	4	616	36	14.3 <sub>+3.3</sub>	3	719	10
258	3	441	8	32.3 <sub>+1.3</sub>	4	473	41	27.4 <sub>+4.8</sub>	3	652	3
290	3	202	17	39.9 <sub>+4.5</sub>	4	231	21	31.3 <sub>+5.6</sub>	3	336	2
292	3	244	2	39.0 <sub>+4.9</sub>	4	247	16	38.3 <sub>+5.1</sub>	3	400	3
324	3	248	2	36.4 <sub>+3.8</sub>	4	256	18	34.4 <sub>+4.5</sub>	3	390	24
326	3	675	11	8.5 <sub>+3.4</sub>	4	618	32	17.9 <sub>+4.0</sub>	3	738	39
360	3	213	7	50.2 <sub>+5.2</sub>	4	227	10	47.0 <sub>+4.8</sub>	3	428	36
362	3	115	7	65.8 <sub>+5.4</sub>	4	153	11	54.6 <sub>+5.1</sub>	3	337	29

No visible trend in the collection efficiency is observed by increasing the contact time or surface area. This was further substantiated by the use of a 500 lb (226 kg) Ventosorb filter. This stabilized the TAGA readings, but did not reduce organic contaminants.

In view of these findings, air may be cleaned by passing through a mixture of Florisil and urethane foam coated with mixed GLC liquid phases. This avenue should be explored in the future.

#### 5.4 Quality Control Samples

In order to establish the validity of analytical data produced by the MOE TAGA<sup>TM</sup>3000 unit, several quality assurance samples were prepared by the Ministry. These samples were analyzed during Phase I when the DSORBA program and the metal GLC injector were in use. Unfiltered outdoor air was chosen as the carrier gas. The syringe drive mentioned earlier was not in use at the time of this analysis. These quality assurance samples were injected discretely with a 10-microliter microsyringe.

##### 5.4.1. Quality Assurance Samples.

Three quality assurance samples were prepared in iso-octane. The composition of these samples were disclosed after the completion of the analysis of these samples by the TAGA<sup>TM</sup> unit. Table 5.11 lists isomers and their concentrations.

TABLE 5.11

**CONTENTS OF THREE  
QUALITY ASSURANCE SAMPLES**

(1) <u>Sample Number 7</u>		<u>Concentration</u>	<u>Total Species Concentration</u>
Monochlorobiphenyl	2-	85.9 ng/ml	85.9 ng/ml
Dichlorobiphenyl	2,2 -	84.1	200.0
	4,4 -	115.9	
Trichlorobiphenyl	2,4 ,5-	99.0	99.0
Tetrachlorobiphenyl	2,2 ,4,6-	152.1	235.0
	2,2 ,5,6 -	82.9	
Pentachlorobiphenyl	2,2 ,4,5,5 -	95.8	95.8
Hexachlorobiphenyl	2,2 ,4 ,5 ,6-	55.9	157.1
	2,2 ,4,4 ,6,6 -	101.2	
Octachlorobiphenyl		68.3	68.3
(2) <u>Sample Number 9</u>			
Monochlorobiphenyl	2-	109.5	
	3-	218.2	418.8
	4-	91.1	
Tetrachlorobiphenyl	2,3,4,5-	98.6	
	2,3,5,6-	112.1	415.8
	2,3' ,4,6-	99.1	
	2,2' ,4,6-	106.6	
Pentachlorobiphenyl	2,2 ,3,4,6-	103.6	
	2,2 ,3,4,5 -	82.2	282.9
	2,2 ,4,4 ,6-	97.1	



TABLE 5.11 (Cont'd)

(3) Sample Number 12

Monochlorobiphenyl		<u>Concentration</u>	<u>Total Species Concentration</u>
	2-	133.0 ng/ml	133.0 ng/ml
Dichlorobiphenyl			
	3,4-	107.4	223.8
	3,5-	116.4	
Trichlorobiphenyl			
	2,3,4-	97.9	
	2' ,3,4-	102.9	302.4
	2,4,5	101.6	
Tetrachlorobiphenyl			
	2,2 ,3,3 -	76.7	
	2,2 ,4,4 -	85.4	340.3
	2,2 ,5,5 -	93.1	
	2,2 ,6,6 -	85.1	

---

#### 5.4.2 Analytical Method

Using Standard Solution #2 (See Section 3.2 5.2) the TAGA<sup>TM</sup> unit was calibrated, and its response factors in terms of ion counts per ng PCB were obtained as follows:

<u>Species</u>	<u>m/z</u>	<u>Response Factor (ions/ng PCB)</u>
Mono	187.5	250.6
	189.5	86.9
DI	221.6	485.4
	223.7	298.5
TRI	255.6	387.6
	257.6	370.3
TETRA	289.6	193.4
	291.6	239.2
PENTA	323.4	185.9
	325.5	286.5
HEXA	359.4	29.2
	361.4	20.2

The ratios of these response factors may be regarded as observed isotopic abundances. These observed values are compared with their calculated values. Except for the hexachlorobiphenyl both ratios are in good agreement (Table 5.12).

TABLE 5.12

COMPARISON OF OBSERVED  
AND CALCULATED ISOTOPIC ABUNDANCE RATIOS

Species	Observed <sup>*</sup> (%)	Calculated(%)
Monochlorobiphenyl	34.7	32.5
Dichlorobiphenyl	61.5	65.0
Trichlorobiphenyl	95.5	97.5
Tetrachlorobiphenyl	80.8	76.9
Pentachlorobiphenyl	66.1	61.5
Hexachlorobiphenyl	69.1	81.2

\*  
=  $\frac{\text{Response factor of 2nd strongest isotopic peak}}{\text{Response factor of strongest isotpic peak}} \times 100$

$$C = \frac{\text{Response of PCB spiked Air (ions)} - \text{Background(ions)}}{\text{Aliquot (ml)}} \times \frac{1}{\text{Response Factor (ions)}} \quad (\text{ng})$$

The concentration of PCBs in the quality assurance samples were calculated by the following equation:

For instance, a 10 microlitre injection of sample 12 produced the 3 readings: 1610, 1713 and 1602 ions, resulting in  $x = 1642$  ions. The background at the same  $m/z$  (255.6) gave 541, 343, 374, and 344 ( $x = 400$ )

$$C = \frac{1642 - 400}{0.010} \times \frac{1}{387.6} = 320.4 \text{ ng/ml}$$

This is close to the actual concentration of  $302.4 \frac{\text{ng}}{\text{ml}}$  disclosed later by the Ministry.

In the same fashion the concentration of each species present in the quality assurance samples was calculated and tabulated in Table 5.13. The observed (experimental) values agree well with the actual concentrations for the tri-, tetra- and penta-chlorobiphenyls. However, the experimental values tend to deviate significantly in the mono-, di-, and hexachlorobiphenyl regions due to the widely varying background fluctuations. The use of a syringe drive should also improve the reproducibility of the signals, since it is difficult to manually inject the accurate amount at exactly the same moment. Those small readings, e.g., 8 and 5 for the trichloro-biphenyl in Sample 9, could originate from the fact that standard chemicals are contaminated with other PCB species, or cross-contaminated during the analysis or preparation of these solutions.

Some discrepancies between the observed and calculated concentrations may be attributed to the difference in isomeric response as discussed in Section 5.2.

TABLE 5.13

Analytical Results of Quality Assurance Samples

Species	m/z	#7		#9		#12	
		Observed	Calculated	Observed	Calculated	Observed	Calculated
Mono	188	0	85.9	830	418.8	389	133.0
	190	322		760		0	
DI	222	178	200.0	48	0	88	223.8
	224	192		55		90	
TRI	256	76	99.0	8	0	320	302.4
	258	89		5		331	
TETRA	290	128	235.0	429	415.8	297	340.3
	292	168		447		324	
PENTA	324	89	95.8	208	282.9	32	0
	326	108		324		36	
HEXA	360	307	157.1	0	0	74	0
	362	404		91		0	

## 6. Stack Simulation Studies (Phase II)

The success of the work reported in the previous section permitted our attention to be turned to the challenging problem of fast-response monitoring for possible PCBs in the stack gas during the test burn, as described in the Test Protocol (Ref. 5).

The hot, steamy and dust-laden composition of the stack gas creates problems in developing and installing an appropriate stack gas sampling system to the TAGA<sup>TM</sup>. It was decided that the work would proceed in two phases, i.e. a Stack Sampling Simulation research study at SCIEX, followed by installation and complete testing of the most appropriate configurations at St. Lawrence Cement.

### 6.1 Design Objectives

- (a) To provide a gas source which matched as closely as possible the stack gas composition, together with an experimental sampling system to permit various approaches to PCB transfer into the TAGA<sup>TM</sup> system.
- (b) To measure all the pertinent PCB transfer characteristics of the most promising approaches tried, in order to assess the feasibility of achieving the required analytic capability and to provide the basic design inputs for the total system to be installed on the St. Lawrence Cement stack.

### 6.2 Experimental Set-Up

As described earlier, the PCBs are collected on an adsorbent-coated wire collector which shuttles between the sampling stream and the TAGA<sup>TM</sup> inlet gas stream. The stack gas parameters presented a development dilemma - would it be better to transfer the hot, steamy, dusty stack gas without any alteration through an inert transfer line to the collector devices, (whose properties could only be guessed at under these conditions) or would it be better to condense the steam, filter out the dust, and cool the sample stream to convenient temperatures? In the latter case the collector probe would be working under proven, known conditions, but

the problem is transferred to determining unequivocally and accurately whether or to what extent PCB transfer down the sampling line would be affected, particularly in the steam condensation process.

Since experiments soon showed that the former choice led to very poor PCB collection efficiency of injected PCBs, effort was focussed on the latter approach. The experimental set-up is shown photographically in Figure 6.1 and schematically in Figure 6.2.

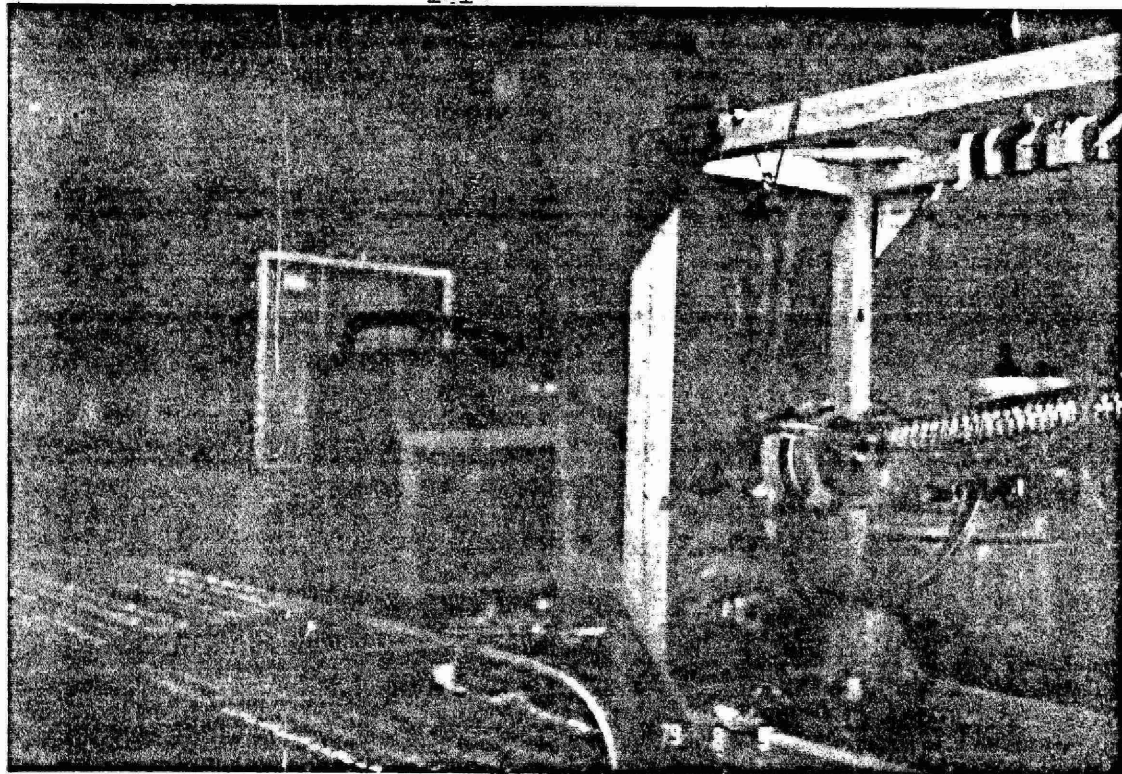
The sampling system is basically an all-glass 19 mm I.D. tubing with minimized Teflon-gasketed connectors, capitalizing on earlier experience that metal parts lead to trouble when trace PCB determination is required. (Ref. 4).

Working from the inlet, the system consisted of an ambient air inlet, a preheater, steam addition from a glass boiler with pure water, a length of heated transfer line, a glass filter (optional), an all glass water-cooled condenser with provision for collection of condensate, the TAGA<sup>TM</sup> sampling position, a flowmeter, sample pump and a charcoal filter to remove PCBs before exhaust. Heaters and thermometers were installed as indicated. PCBs could be accurately injected at the positions shown, so that comparison of amounts reaching the TAGA<sup>TM</sup> could permit evaluation of transfer coefficients down lengths of line and through the condenser, and the effect of temperature on response time when changes in inlet PCB concentration occurred.

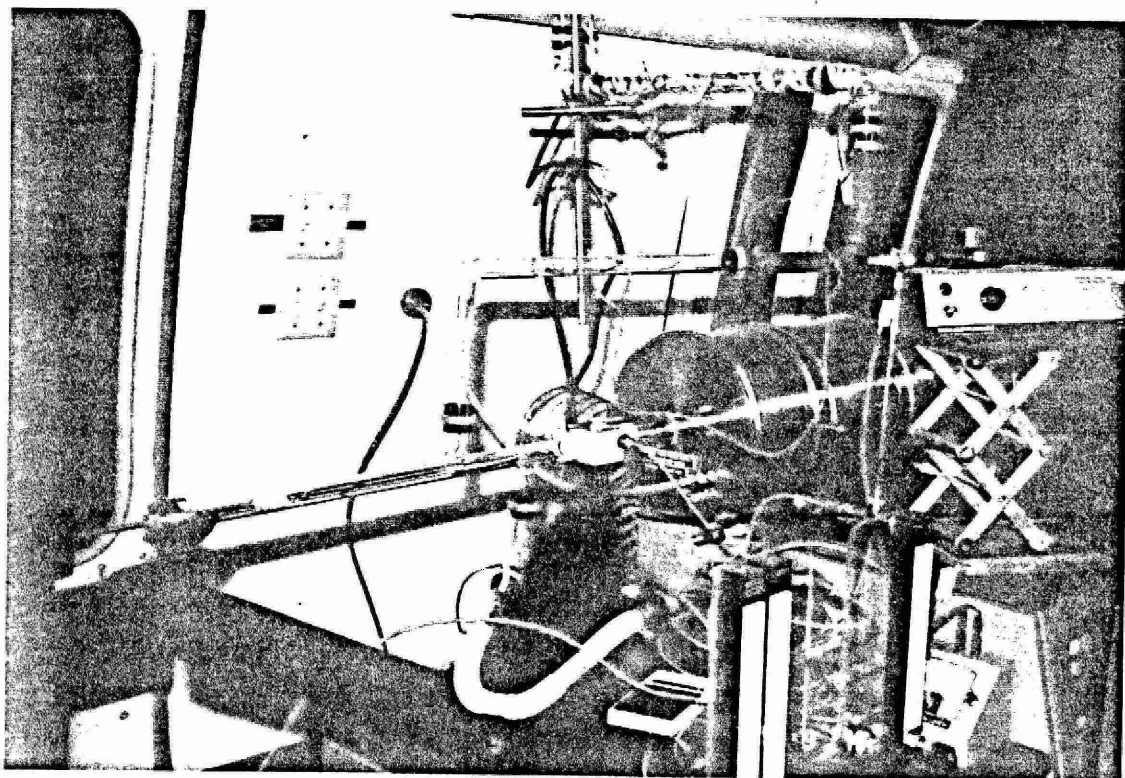
The simulation was as complete as was feasible.

To summarize:

- the steam fraction was about 15% (compared to 35% at the stack), enough to demonstrate any co-condensation of PCBs.
- temperatures were matched to stack conditions
- no dust simulation was feasible
- since no real knowledge of the trace organic composition of the stack gas existed, the possible effect of this on detectability limits for the PCBs could not be studied.



CONDENSER ON ROOF

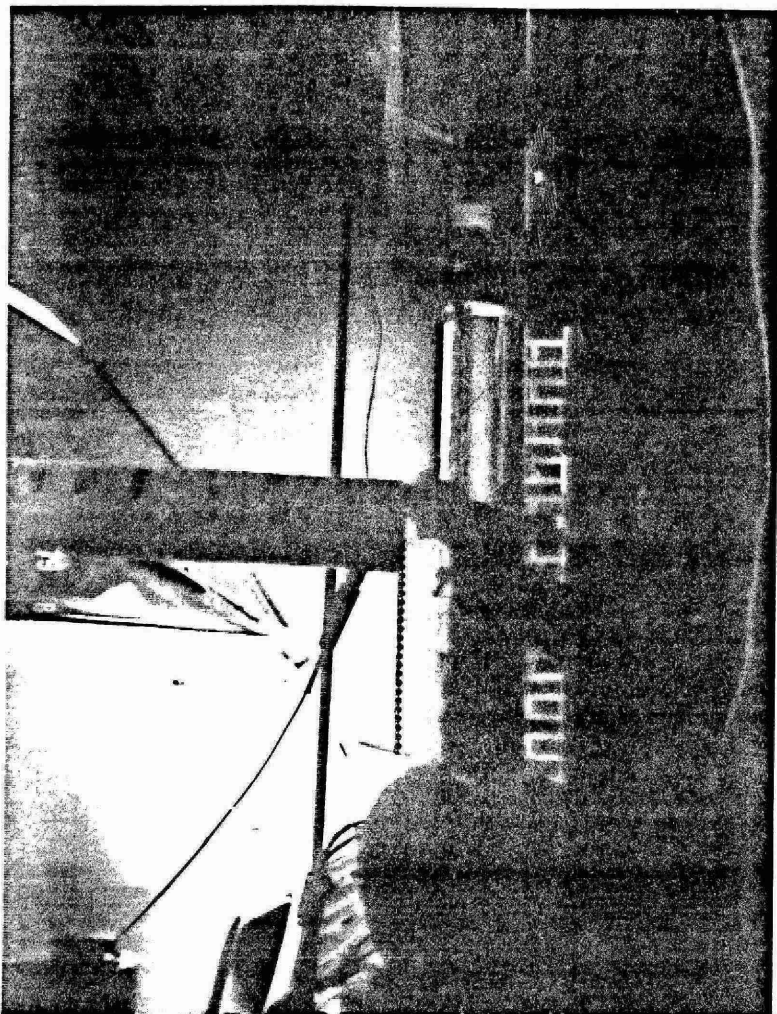


INTERIOR LINE TO TAGA

PHOTOS OF STACK SIMULATION TEST

FIGURE 6.1

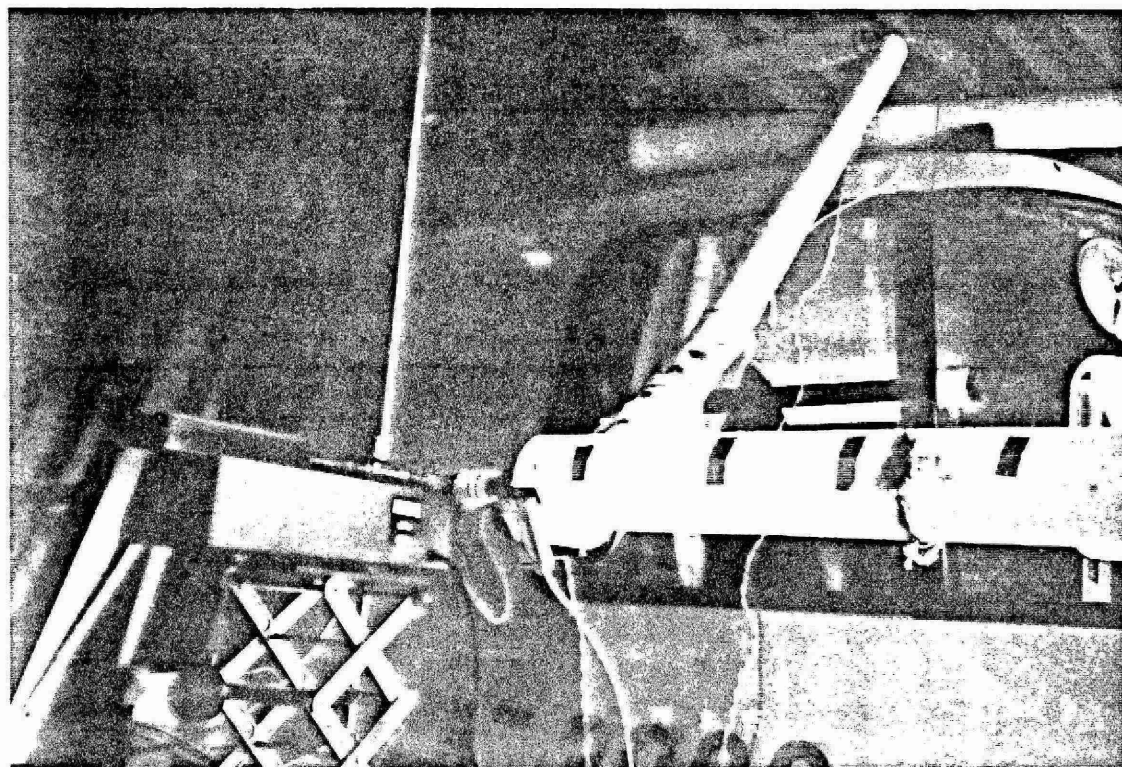




..... Continue Figure 6.1

Left: INLET AND STEAM  
BOILER

BELOW: DETAIL OF PCB INJECT  
AND LINE CONSTRUCTIO  
AND TRANSFER LINE



PHOTOS OF STACK SIMULATION TEST  
FIGURE 6.1 cont'd

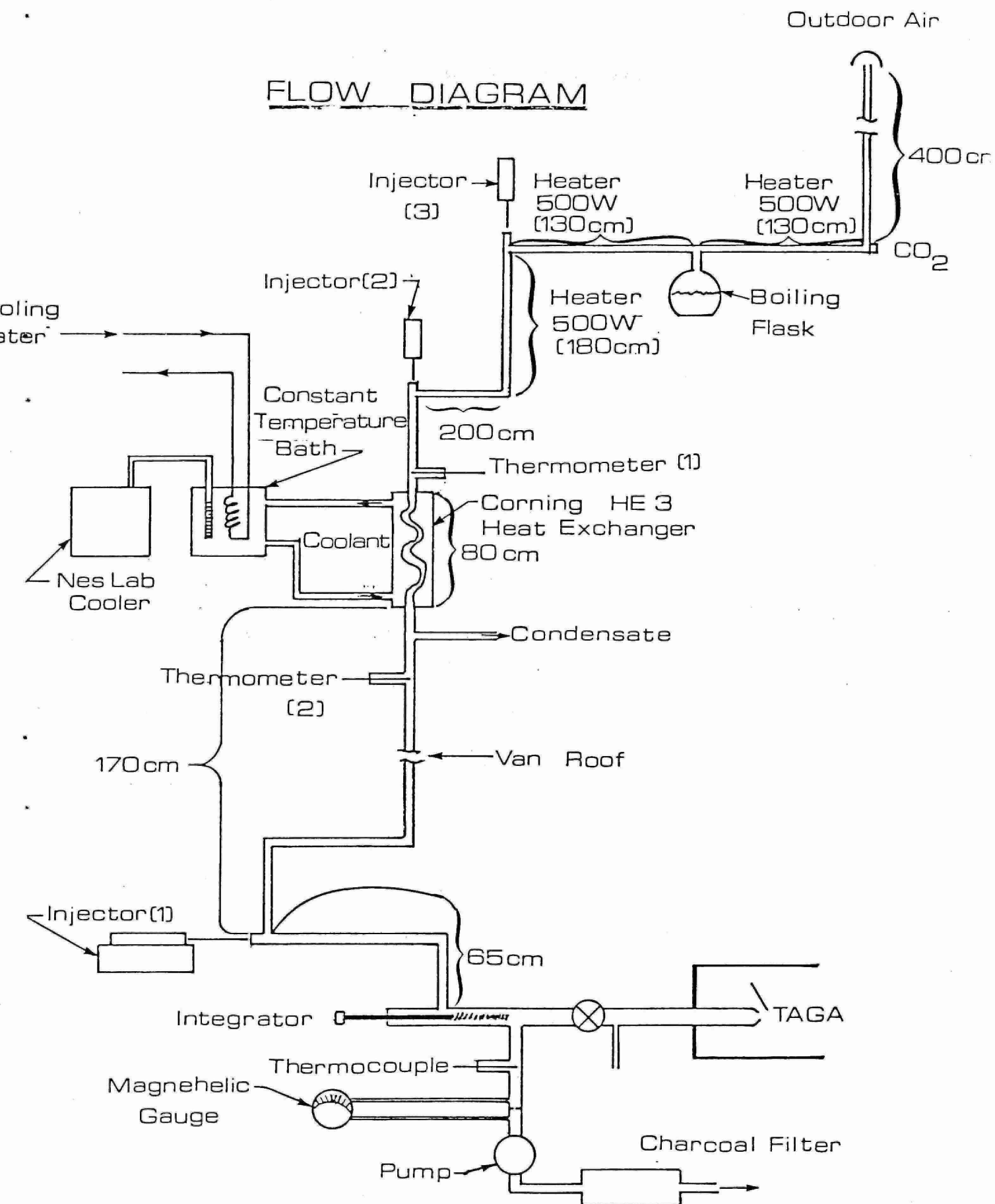


Figure 6.2

To crosscheck on the possibility of removal of PCBs in the steam condenser, the condensate was collected during each run and sent to the MOE Pesticides Laboratory for PCB determination.

### 6.3 Balston Filter Test

A Balston filter assembly, Type 30/25, 1 7/8" (47.6 mm) diameter x 8 3/4" (222.3 mm) high, filter tube 1" x 7" (25.4 mm x 177.8 mm) was manufactured by Balston, Inc. Lexington, Massachusetts, and supplied to SCIEX by the Ministry. This filter had been extensively used by the Ministry to sample stack gases. Thus, it was important to evaluate whether this filter can be used for subsequent PCB analysis.

The stainless steel Type 304 assembly was thoroughly washed with detergent, water, acetone and water, and baked in an oven at 200°C for 3 days prior to this experiment.

At the beginning this filter was inserted in the test line (See Figure 6.2), in place of the Corning HE3 Heat Exchanger, using 1/2" (12.7 mm) I.D. Teflon tubes. However, these tubes permeated organic matter upon heating. Therefore, these tubes were replaced with Kovar seals of the same diameter. The assembly was wrapped with heating wires. At first, a number of background readings were obtained for outdoor air, when no heat was applied to the probe. Then, known amounts of PCBs were added to the sample line through a heated glass injector just upstream of the TAGA<sup>TM</sup> unit to examine the total system's response.

Then, the Balston filter unit (with a fibreglass element in place) was heated at 234°C. After the temperature of the filter became steady, a number of adsorption/desorption cycles were repeated to obtain a new set of background readings, which turned out to be much higher than the previous background when no heat was applied to the Balston unit. When PCBs were added to the system, there was virtually no significant increase in the TAGA<sup>TM</sup> response. This observation is tabulated in Table 6.1. The analysis was focussed on the hexachlorobiphenyl, because a very similar experiment carried out a few days prior to this experiment did

TABLE 6.1

### BALSTON FILTER TEST

[illegible]

not produce any positive response when known amounts of PCBs were added to the sample line in the presence of the hot Balston filter holder (less filter element), and since this species was the heaviest species present in the standard solution, it should be the most thermally stable species. At the time of this experiment a heat exchanger was not used, and the PCB wire integrator was operated at approximately 100°C, when the Balston filter was heated at 234°C. The lack of positive response to the added PCBs could be attributed to the thermal behavior of the PCB wire integrator or to the active surface of the stainless steel probe.

As soon as the steel probe was heated, and the PCB integrator temperature remained constant at about 50°C, a rapid increase in background reading was observed on several occasions. Thus, it was decided that this Balston probe was not suited to our stack monitoring.

#### 6.4 Heat and Steam Test

In Section 6.2 we presented a development dilemma, i.e., would it be better to transfer the hot, steamy, dusty, stack gas, without any alteration, through an inert transfer line to the collector device or would it be better to condense the steam, filter out the dust, and cool the sample stream to convenient temperatures. An experiment was designed to answer this question. In this experiment, the heat exchanger shown in Figure 6.2 was replaced with a heat traced 19 mm I.D. glass tube. At first the whole line was kept at ambient temperature except for the heated glass injector, immediately upstream of the PCB wire integrator (Injector 1 in Figure 6.2). A number of background readings were obtained at a PCB integrator temperature of 50°C. Then, known amounts of PCBs were added through Injector 1 to obtain the system's response factors for 10 PCB peaks. Then the syringe was removed and heat was applied to the entire sample line to make the integrator temperature at 80°C. After obtaining the stable temperature background readings, known amounts of PCBs were measured to obtain a new set of response factors in ions/ng at 80°C.

The syringe was again removed from Injector 1, and a few background readings were measured. Then, steam was added to the system at 35-43 V/V % using a kettle. Although this technique had been expected

to produce a constant temperature due to the latent heat of evaporation of the water, it was found difficult to control the temperature of the integrator region at 86-100°C. The water vapor either condensed too quickly or was overheated. The thermocouple registered 80-125°C with occasional temperature excursions as high as 160°C. Background readings as well as responses to the added PCBs were measured to obtain response factors. Table 6.2 summarizes these results, i.e., response factors (ions/ng PCB), when the integrator temperature of 50°C (dry), 80°C (hot and dry), and 80-125°C (hot and wet). Table 6.3 compares trapping efficiencies relative to those obtained at 50°C and dry air, that is, outdoor air. The PCB wire integrator collects only 10-30% at 80°C and almost no collection efficiency was observed at 80-125°C with steam. For these reasons this approach was abandoned.

A Corning heat exchanger, HE3, was installed to condense the steam and cool the sample stream to 50°C at the point of sample collection. (See Figure 6.2). In this case the PCB wire integrator would be working under proven conditions. The problem is to determine whether or to what extent PCB transfer down the sampling line would be affected, particularly in the steam condensation process.

#### 6.5 Effect of Temperature on Response Time to PCB Concentration Change

In these tests the di- to hexa-chloro PCBs were monitored, since it was suspected that the heavier, less volatile PCBs would be more proven to "stick" on any cold spot in the line.

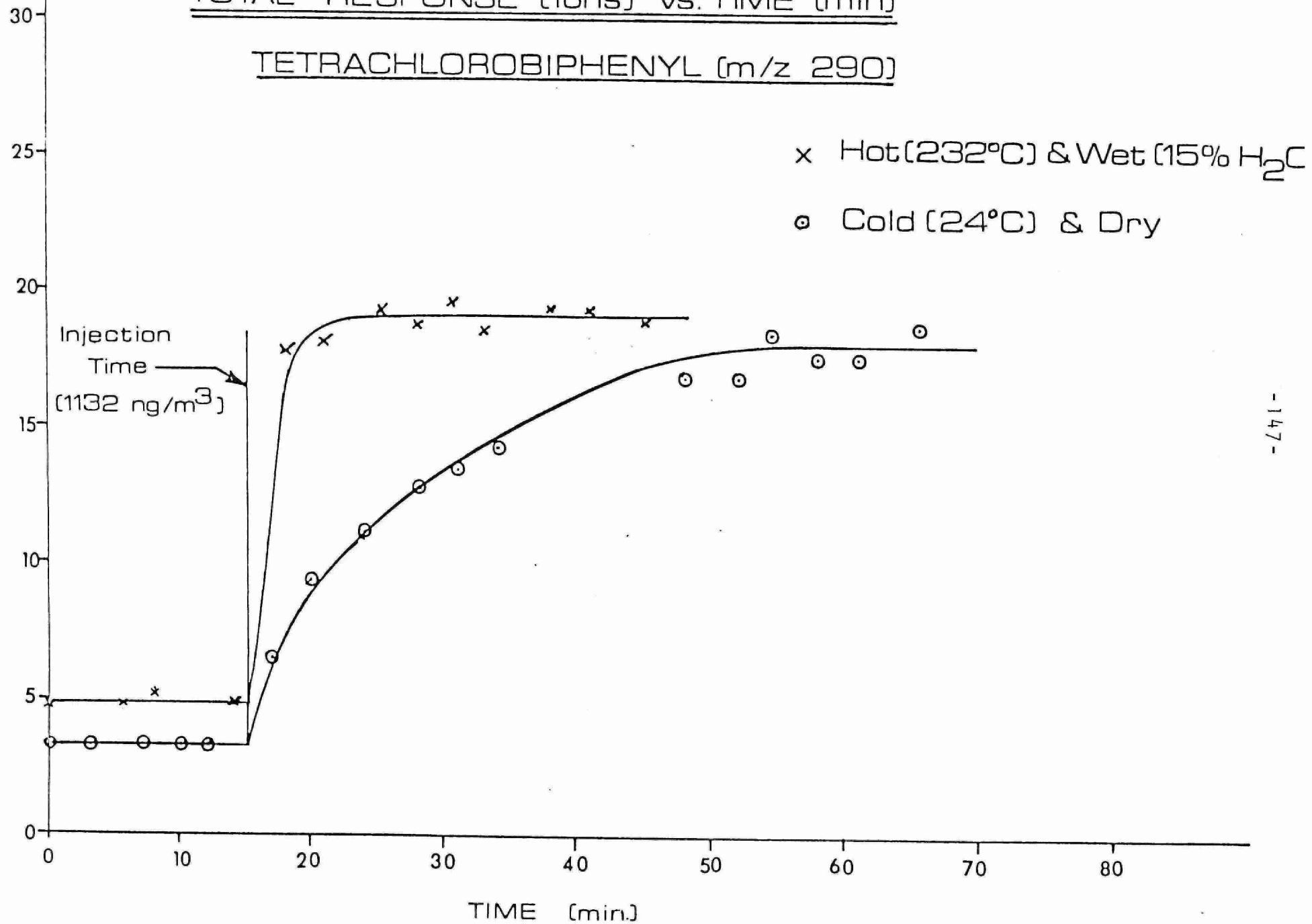
Figure 6.3 illustrates, by starting a steady injection of PCBs at time zero, how the transmitted PCB flows build up to the steady state volume. Comparison of the data taken at hot and cool line temperatures shows that it is important to control condenser operations and line heat losses so that areas below 30°C do not occur, otherwise long response times are produced.

It was also shown clearly that the sample gas emerging from the condenser must be reheated slightly in order to move it away from

TOTAL RESPONSE [Ions] vs. TIME [min]

TETRACHLOROBIPHENYL (m/z 290)

TOTAL RESPONSE (IONS  $\times 10^{-3}$ )



the saturation point and prevent the remaining water from condensing in the lines or on the collector probe. A condenser outlet temperature of 30°C and a small reheat to 50°C was found to be appropriate.

#### 6.6 PCB Transfer Coefficients Through Condenser

By moving the PCB injector from 170 cm downstream of the condenser to immediately upstream of the condenser (See Fig. 6.2), and noting the steady state response of the TAGA<sup>TM</sup> 3000 to identical injection rates of PCBs, the condenser transfer coefficients were obtained as tabulated in Table 6.4.

The condensate was collected during each of these runs in clean glass bottles prepared by the Ministry of the Environment and later analyzed by the Pesticides Section of the Ministry.

The results show conclusively by both approaches that the maximum co-condensation or water-grabbing of PCBs in the steam condensation process is in the range of 1 to 3%. This very important positive result permits a stack sampling configuration with pre-condensation of steam before PCB collection. The result is not unexpected, being consistent with the maximum concentration of PCBs in the water sample calculated from their known very low solubilities in water.



TABLE 6.2

COMPARISON OF BACKGROUNDS RESPONSES AND RESPONSE  
FACTORS AT DIFFERENT TEMPERATURES AND HUMIDITIES

SPECIES	DI		TRI		TETRA		PENTA		HEXA	
m/z	222	224	256	258	290	292	324	326	360	362
a Background (ions) 50°C, dry n=5	5278	5074	3980	3104	904	1267	906	1325	7105	9059
a PCB (ions) 50°C, dry n=3	15139	11145	11035	9812	5055	6584	4964	7377	55936	40783
Response Factor (ions/ng) 50°C dry	200	123	102	97	46	59	54	81	291	189
Background (ions) 80°C, dry n=3	4640	3214	2663	2778	1710	2145	6121	14124	44866	53183
b PCB (ions) 80°C dry	6234	4356	3590	3508	2189	3100	7493	16007	37970	46295
Response Factor (ions/ng) 80°C dry	33	23	13	11	5	11	18	25	0	0
Background (ions) 80-125°C, wet, N=4	3646	3316	2205	3048	1153	1520	1524	4300	17918	31549
c PCB (ions) 80-125°C, wet n=2	3445	3951	2090	2879	1089	1469	1503	6318	15751	32970
Response Factor (ions/ng) 80-125°C, wet	0	13	0	0	0	0	0	27	0	34

N: Number of measurements

TABLE 6.3

**COMPARISON OF TRAPPING EFFICIENCIES**  
(Based on result obtained at 50°C, dry)

SPECIES	DI		TRI		PENTA		PENTA		HEXA	
m/z	222	224	256	258	290	292	324	326	360	362
a	100	100	100	100	100	100	100	100	100	100
b	17	19	13	11	11	19	33	31	0	0
c	0	11	0	0	0	0	0	33	0	18

- a) Response factors at 50°C, dry, converted to 100%.
- b) Response factors at 80°C, dry, divided by corresponding response factors at 50°C, dry; then multiplied by 100.
- c) Response factors at 80-125°C, wet; divided by corresponding response factors at 50°C, dry; then multiplied by 100.

TABLE 6.4

PCB TRANSFER THROUGH  
CORNING HE3 CONDENSER

<u>TEST</u> <u>CONDITIONS</u>	<u>PCB</u> <u>SPECIES</u>	<u>INJECTED</u> <u>CONCENTRATION</u> (ng/m <sup>3</sup> )	<u>TRANSFER</u> <u>TAGA</u> <sup>TM</sup> (+ 0.1)	<u>COEFFICIENT</u> MOE (condensate) <u>analysis</u>
Temperature upsteam of condenser 232°C	di	621	1.0	0.989
	tri	875	1.0	0.986
Temperature downstream of condenser 24°C	tetra	1132	1.0	0.988
	penta	946	1.0	0.968
	hexa	2124	1.0	0.990

6.7      PCB Transfer Coefficients Down Heated Glass Line

A similar test was performed to determine transfer coefficients for long glass heated pipes, since over 25 m of line would be involved at St. Lawrence Cement. As long as the lines were kept hot ( $\approx 120^{\circ}\text{C}$ ) the coefficients did not depart measurably from unity. This is shown in Table 6.5. In this experiment steam (14-15% V/V) and carbon dioxide (approximately 5%) were added to the simulation line.

6.8      Linearity of Total System Response  
Over a Range of PCB Concentrations

The PCB injector was moved to its position closest to the inlet, so that the PCBs were mixed with steam air and flowed down the longest line length (7 m) available and through the condenser to the TAGA<sup>TM</sup>. The linearity of response to concentrations between  $100 \text{ ng/m}^3$  and  $1000 \text{ ng/m}^3$ , shown in Figure 6.3 is excellent, providing assurance that in the general working range of interest no spurious sampling artifacts are being introduced.

Figure 6.4

NET RESPONSE vs CONCENTRATION

TRICHLOROBIPHENYL (m/z 256)

HOT (232°C) & WET (15%)

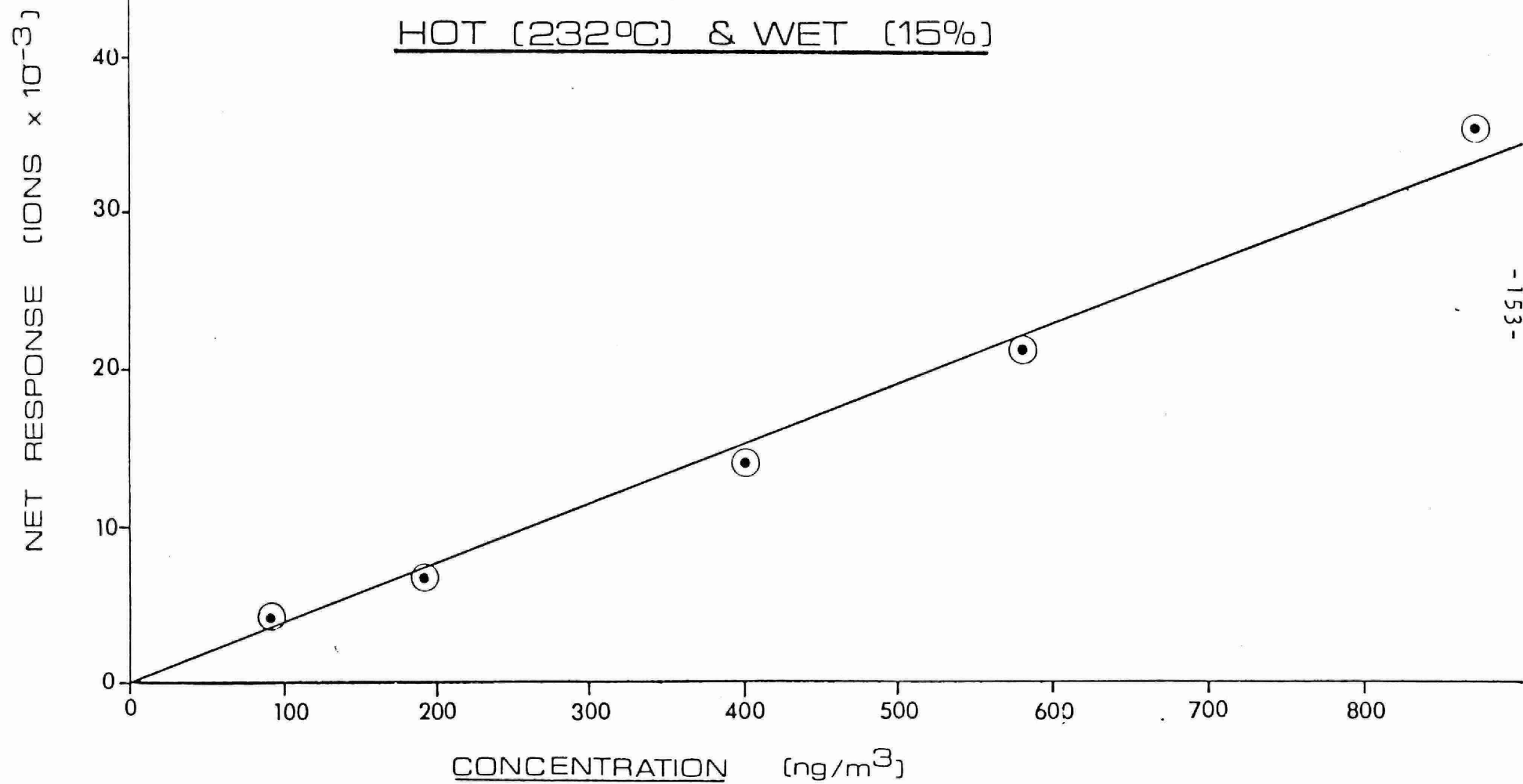


TABLE 6.5

PCB TRANSFER THROUGH HEAT TRACED SIMULATION LINE

	222	224	256	258	290	292	324	326	360	362
Background	11837	10981	9799	8005	6685	8218				
Injection in Van	24917	19545	26888	23957	17082	21017				
Response	13080	8564	17089	15952	11117	12799				
Response Factor										
Background	11837	10981	9799	8005	6685	8218				
Injection at Injector 3	22803	18154	23845	21339	16158	19652				
Response	10965	7173	14046	13334	9473	11434				
Comparison of Response Factors (% difference)	16	16	18	16	15	11				
Overall error: 12%										

Note: data for m/x = 360,362 was not collected and m/z = 324,326 exhibited chemical interference on this particular day.

6.9 Recommendations Based on Simulation Study

As a result of this stack simulation study the following recommendations were made for the fast-response PCB monitoring of the St. Lawrence Cement stack gas during a test burn.

- (1) The sampling line at St. Lawrence Cement should be an all-glass, Teflon-gasketed, and employ pre-condensation of steam before PCB collection. Heating and/or insulating should be provided and the condenser operated so that wall temperatures do not drop below 30°C, and there should be moderate reheat between the condenser and sampling position.
- (2) The line diameter (19 mm I.D.) and sample flow rate (2.2 litres/sec) used in these tests proved to be entirely adequate, but in scaling up to the stack installation it would be prudent to use somewhat larger diameters and flow rates.
- (3) Any filters necessary to remove the dust should be all glass and maintained at the necessary elevated sample temperature.

7. STACK SAMPLING AT ST. LAWRENCE CEMENT

In this Phase III initial objectives were laid as follows:

- (a) Based on the best information resulting from the stack simulation program described in the previous Chapter, design and install a stack sampling system appropriately connected to the MOE TAGA<sup>TM</sup> 3000 van.
- (b) Run preparatory tests to study any effect not covered in the simulation work, notably the effects of dust, stack depression below ambient pressure, and trace organics in the stack gas.
- (c) Document the overall response characteristics (sensitivity, response time, and minimum detectability limits) for the total system using known PCB concentrations obtained by known PCB injection rate at the head of the sampling line.

The design and installation of the sampling line were carried out by the Source Assessment Unit of the Ministry in co-operation with Pegasus Industries of Agincourt, Ontario. Most of the materials used to assemble the sampling line were processed from Pegasus Industrial Specialities Limited and Chemlex of Canada in Rexdale, Ontario.

#### 7.1 Preliminary Sampling Lines

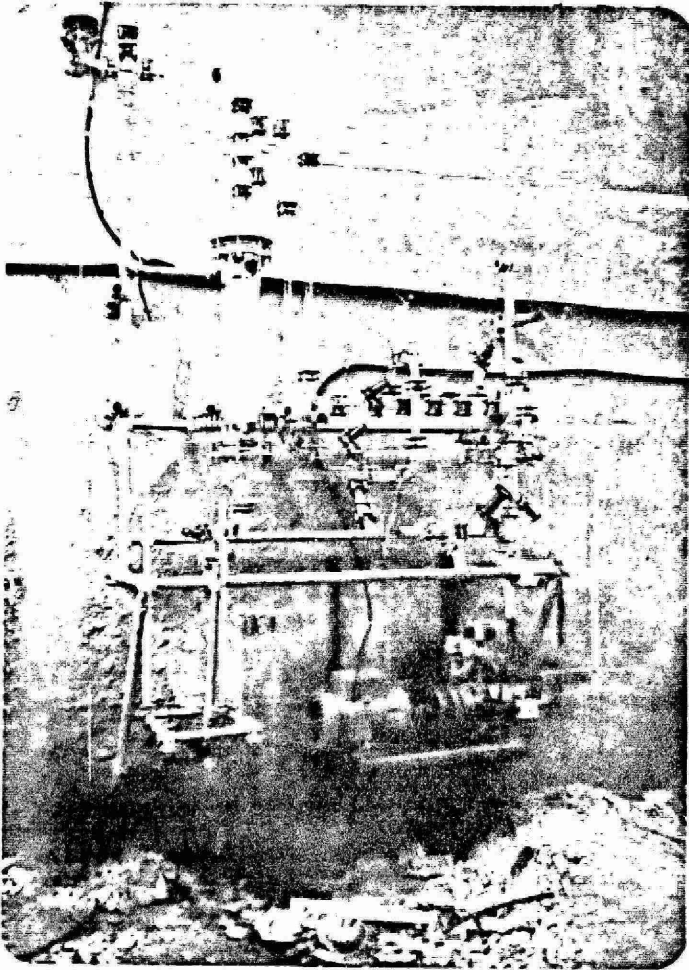
The basic stack installation is shown photographically in Figure 7.1. The sampling line is an enlarged version of the simulation system using

- (i) more rugged one-inch (25.4 mm) I.D. glass tubing with teflon gaskets (Corning Industrial Glass)
- (ii) heavier vacuum pumping (GAST, Model 5565-V6-T338) 26 l/s at 760 mm Hg (no pressure depression)
- (iii) efficient, weatherproof insulation
- (iv) a redesigned preheater - injector system (Figure 7.2): Heating tape was used to maintain temperatures above 120°C, between the duct and the condenser, and to reheat the sample after condensation at 50°C-70°C. Reheating was necessary to obtain optimum PCB transmission between the condenser and the PCB wire integrator. A schematic of the first stack sampling prototype is shown in Figure 7.3. Values 1,2,5,6,7 were open and V3, V9 closed. V8 was partly open to adjust the total flow rate.

The first attempt to monitor stack effluent was made without dust filtering, however, it became evident that the dust coating on the adsorber coil hindered PCB adsorption; thus the following filtering techniques were investigated:

- (1) glass wool plugs
- (2) fritted disk with backflush cleaning





CONDENSER AND SAMPLE  
HANDLING SYSTEM



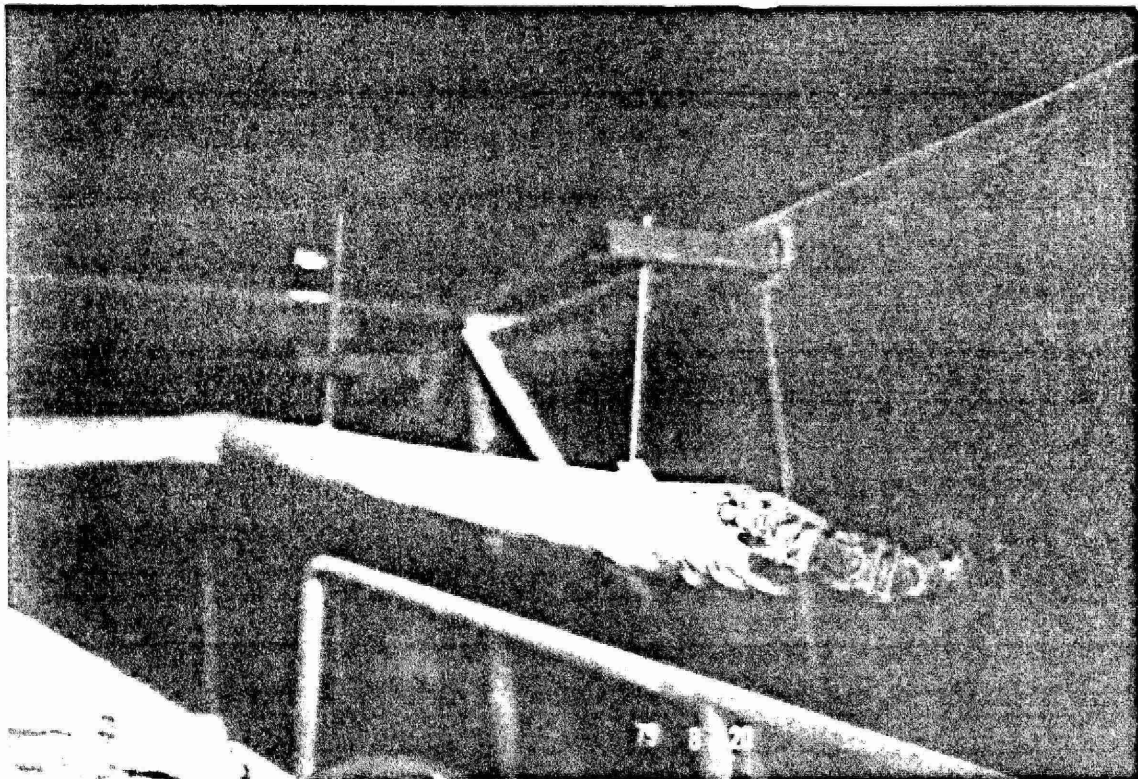
VAN AND TRANSFER LINE

PHOTOS OF PRELIMINARY STACK SIMULATION TEST  
FIGURE 7.1

....Continue Figure 7.1

OPPOSITE:  
VAN AND SAMPLE TRANSFER LINE  
FROM STACK

BELOW:  
SAMPLING PORT ON STACK



PHOTOS OF PRELIMINARY STACK SIMULATION TEST  
FIGURE 7.1

## SCHEMATIC of SOLUTION INJECTION PORT

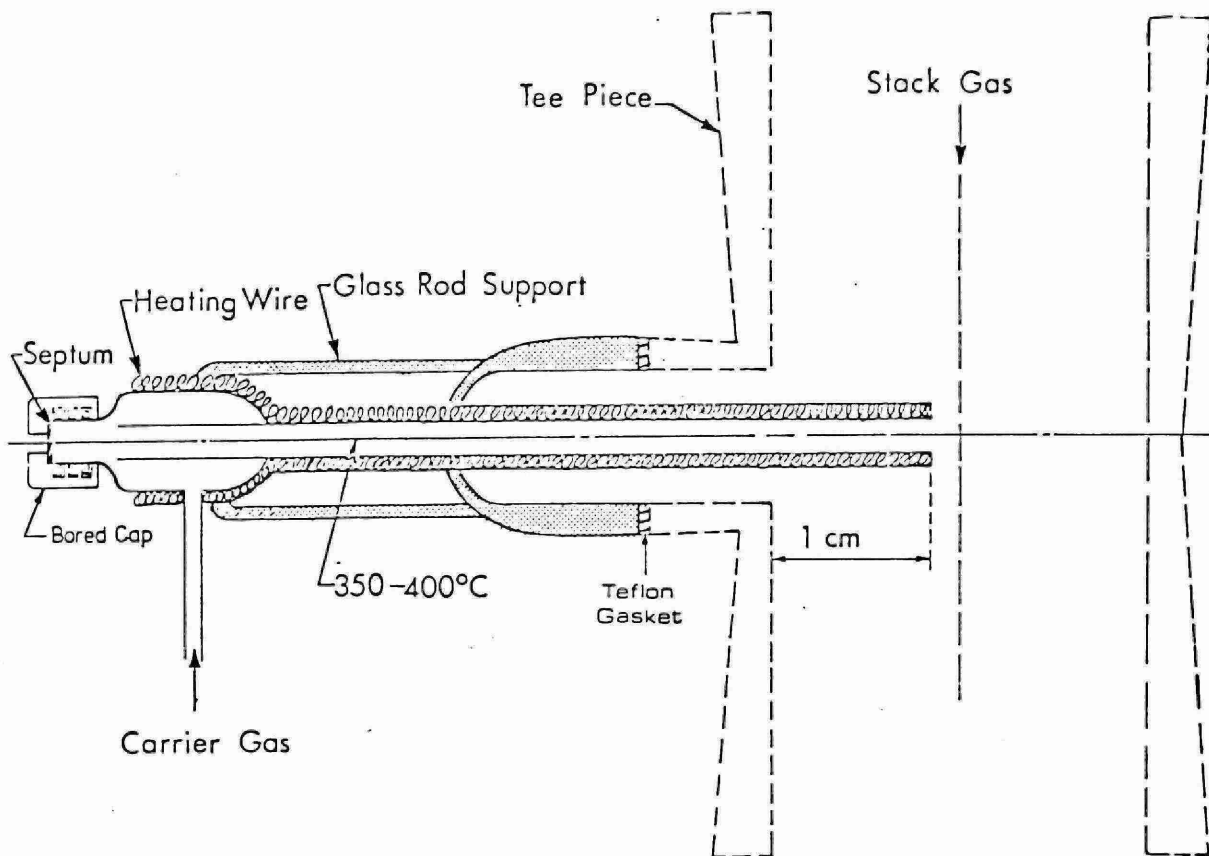
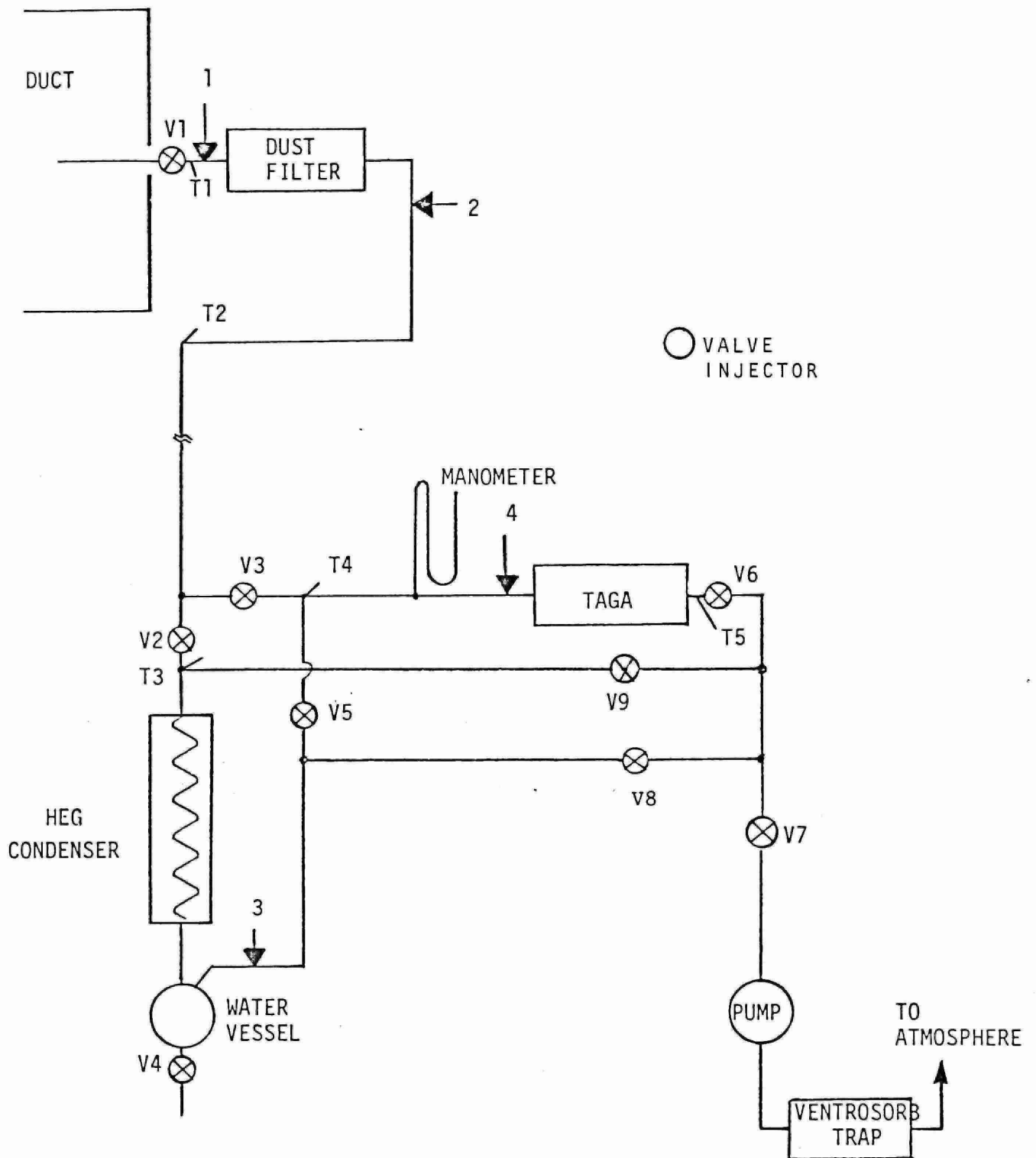


Figure 7.2



SCHEMATIC OF PRELIMINARY STACK SAMPLING SYSTEM

FIGURE 7.3

(3) fritted quartz cylinder

(4) cyclone precipitator

#### 7.1.1 Glass Wool Filters

Initial attempts to filter dust entailed the placement of a small plug of glass wool just upstream of the temperature well at the duct. (Figure 7.4) Other methods of support for the plug were devised. One method involved the use of a wafer of coarse fritted glass sandwiched between teflon gaskets in a pipe joint. The most satisfactory support technique employed the dimpled duct tube shown in Figure 7.5

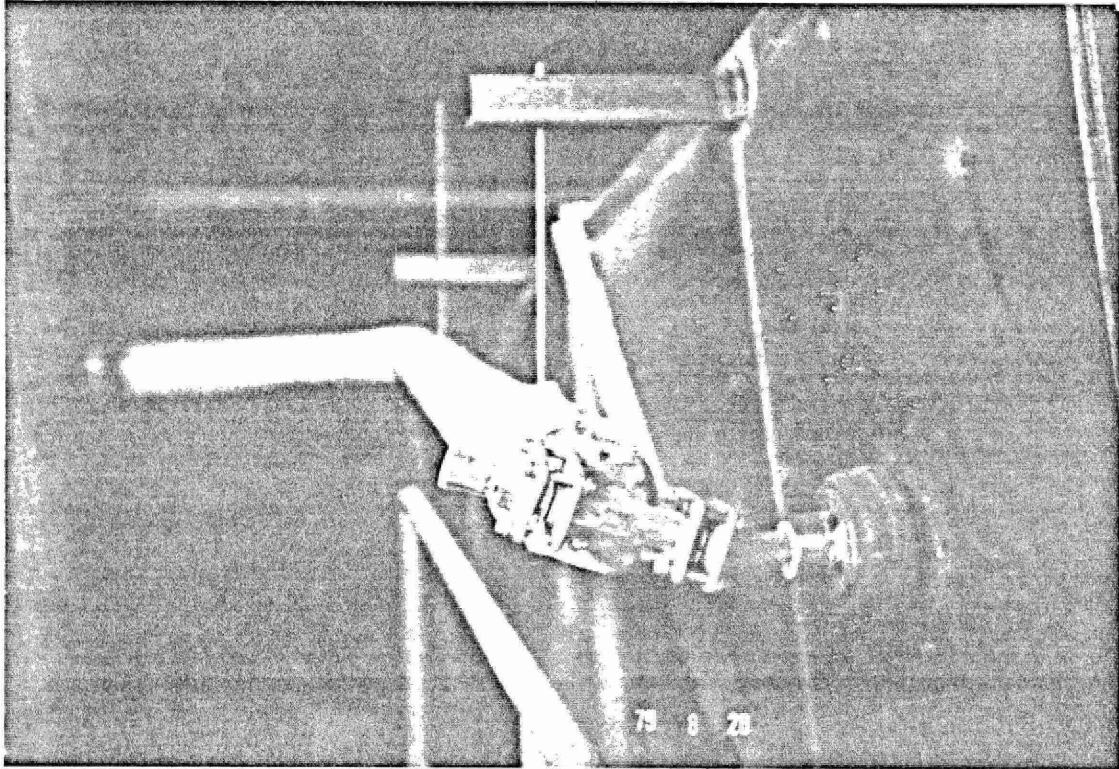
#### Experimental Results and Data

Ion signals at the m/z valves of interest to PCBs were approximately 4-10 times as intense in 100%, filtered stack gas as in ambient air, and less reproducible ( $\pm 30\%$ ). In addition, ambient air sampled through the hot (ca.  $100^{\circ}\text{C}$  before condenser, ca.  $70^{\circ}\text{C}$  after) sampling line yielded ion signals 1.5 to 2.4 times the intensity of those from cold ambient air (Table 7.1).

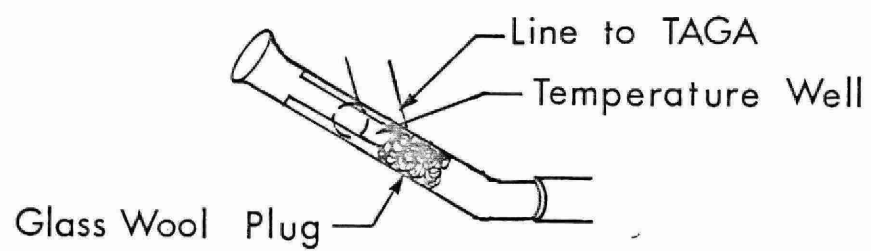
First injections of PCBs were made just upstream (ca. 40 cm.) of the wire integrator and marginal detection of ca.  $7000 \text{ ng/m}^3$  total PCB was observed in 100% stack gas. Glass wool filtration was extremely limited by the very rapid clogging of the filter, that is over the course of one hour of sampling at 1.7 l/sec the pressure depression of the sampling line increased from 2.5 cmHg to greater than 40 cmHg as measured downstream of the condenser. (See Figure 7.3)

#### 7.1.2 Fritted Disc with Backflush Cleaning

In an attempt to reduce the amount of down-time associated with the cleaning of the filter, a coarse fritted disk, 10 cm. in diameter, was inserted into the sampling line near the duct. (Figure 7.6) The valve installed immediately downstream of the filter, helped to provide the reverse gas flow for cleaning.



(a) Photo



(b) Schematic (flanges omitted)

## GLASS WOOL FILTER

Figure 7.4

FIGURE 7.5 DIMPLED DUCT TUBE

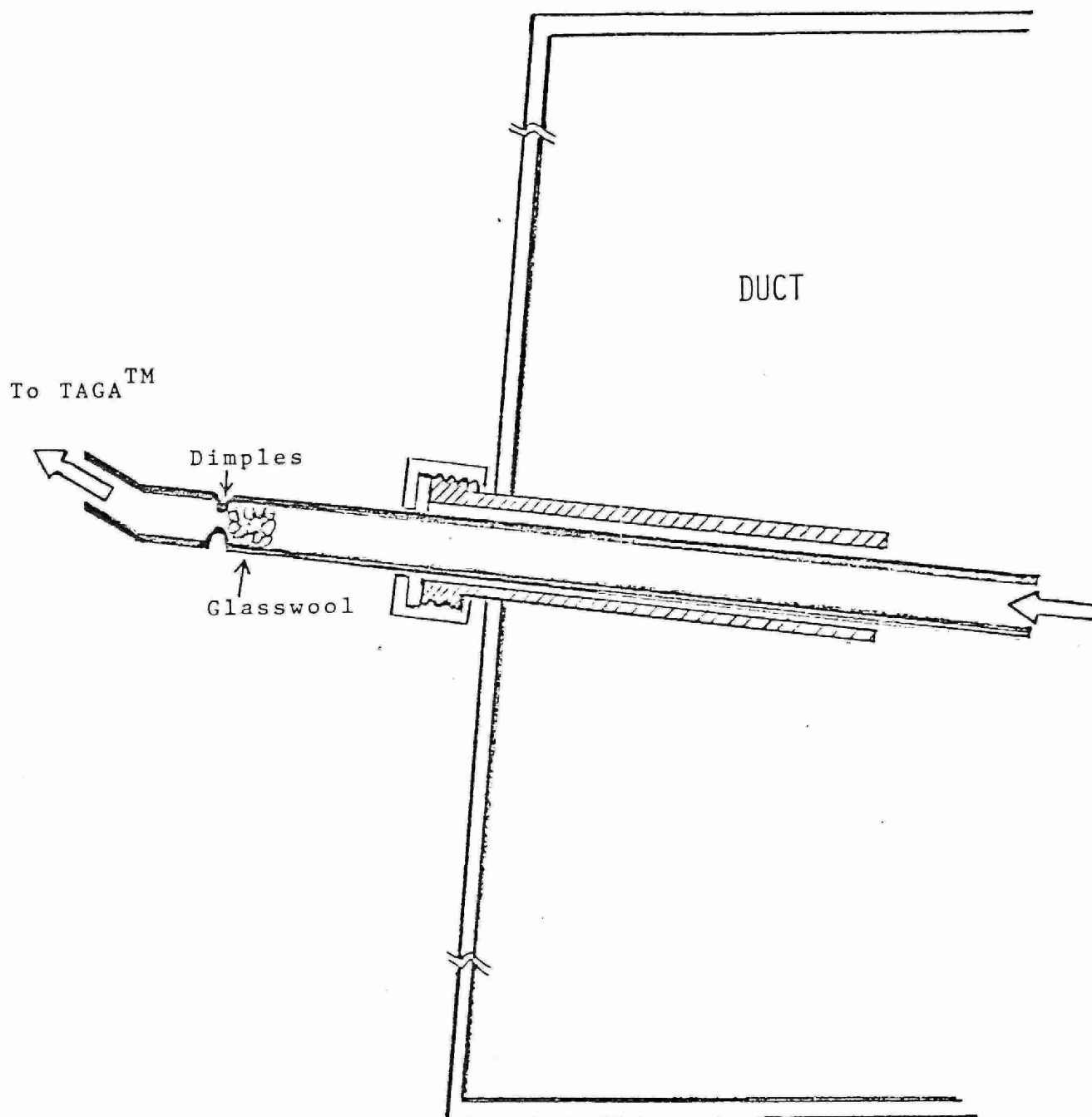
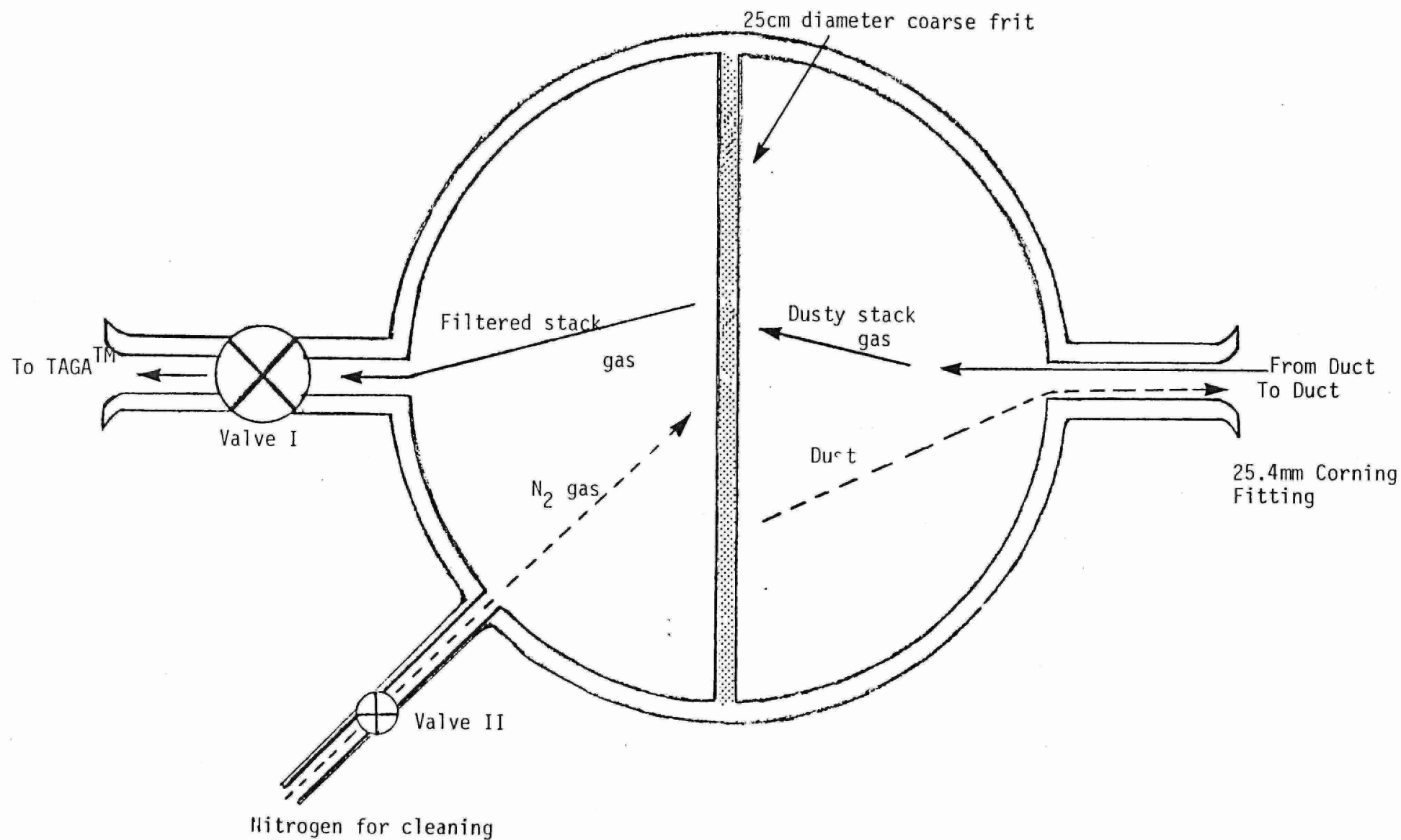




FIGURE 7.6 FRITTED DISC WITH BACKFLUSH CLEANING



To sample: V1, open; V2 closed, flow indicated by solid arrows  
 To backflush: V1 closed, V2 open, flow indicated by dotted line



TABLE 7.1

OUTDOOR AIR RESPONSES THROUGH COLD AND  
HOT SAMPLING LINE

	MONO		DI		TRI		TETRA		PENTA		HEXA	
m/z	188	190	222	224	256	258	290	292	324	326	360	362
Cold Line	4965	5683	10210	9422	7735	5801	3239	3509	14331	24479	10509	684
Hot Line	7928	10100	18080	17689	15549	14072	6660	5397	27182	38576	16612	1238
Ratio*	1.59	1.78	1.77	1.88	2.01	2.43	2.06	1.54	1.90	1.58	1.58	1.8

$$\text{Ratio} = \frac{\text{Response of Outdoor Air Through Hot Line}}{\text{Response of Outdoor Air Through Cold Line}}$$

### Experimental Results

After approximately 3 hours of sampling at 1.7 l/sec the pressure depression exceeded 30 cmHg and backflushing with nitrogen had a negligible cleaning effect. This technique was abandoned as the clogging time was prohibitively short and backflushing would not clean uniformly.

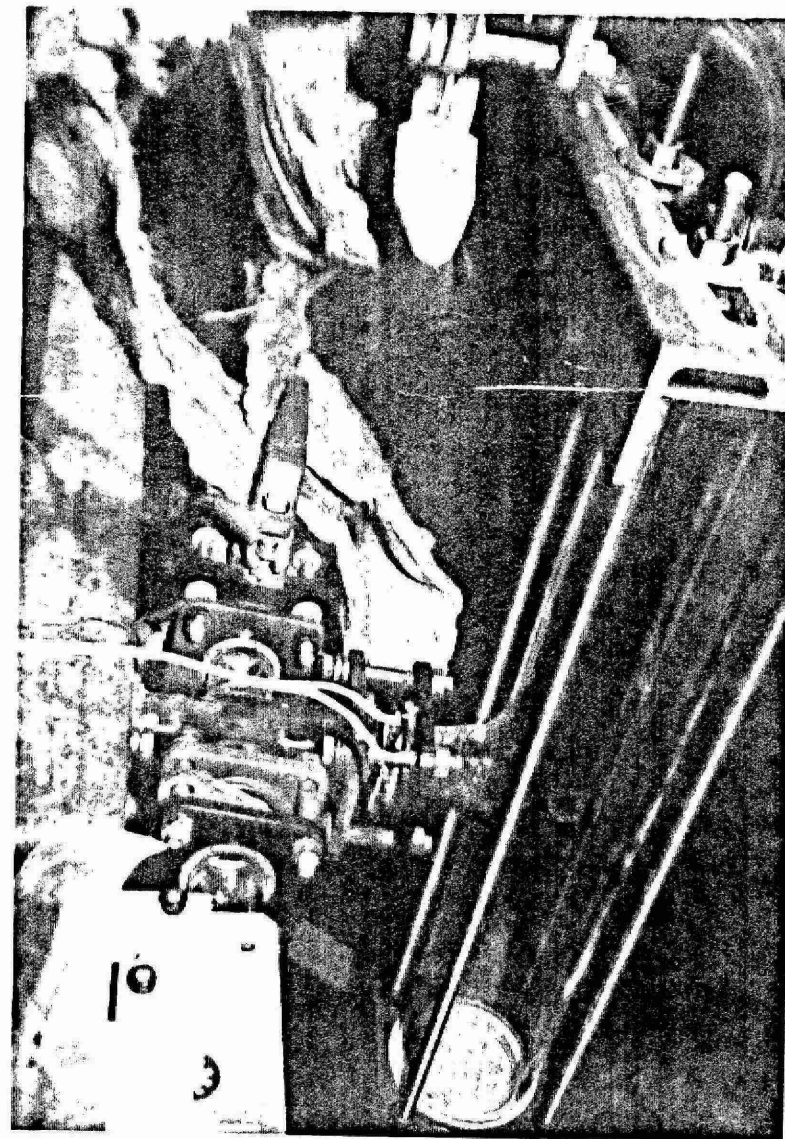
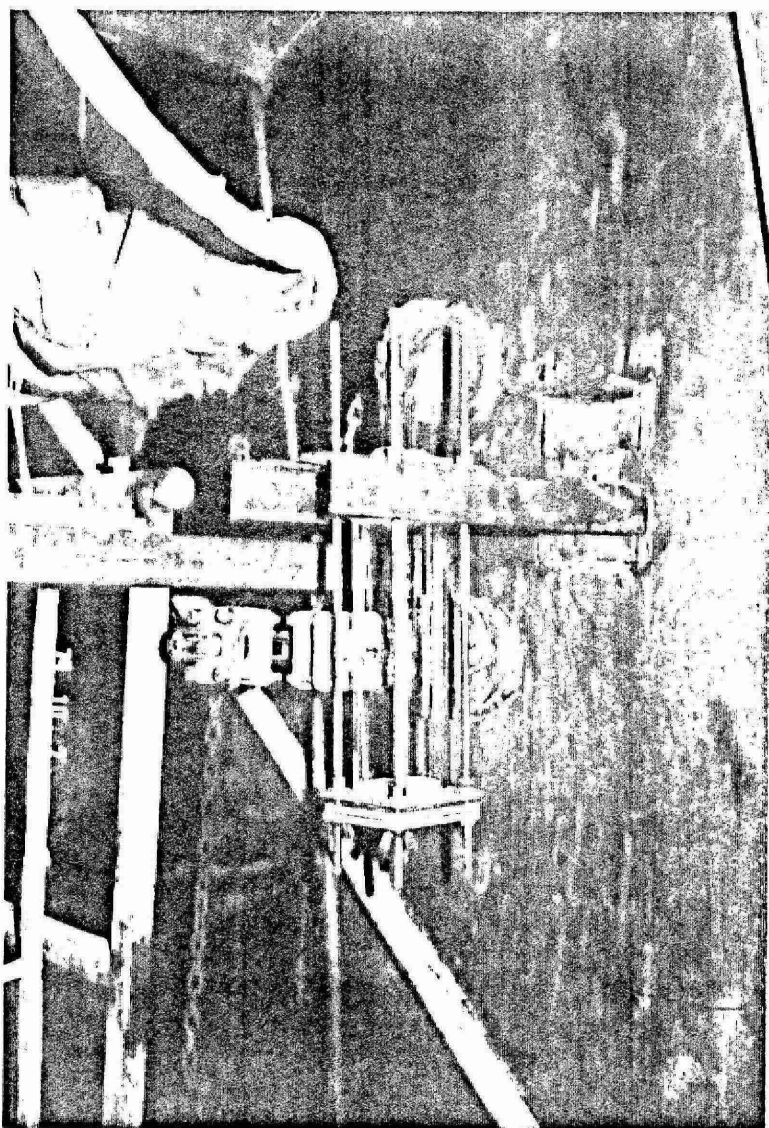
#### 7.1.3 Fritted Quartz Filters

The need for a filter of large surface area was recognized, since it would reduce the frequency of cleaning procedures; in addition, the depression could be minimized with as large a pore size as was practical under the constraints of the filtering requirements.

The fritted quartz filter holder was installed near the duct as is shown photographically in Figure 7.7 and schematically in Figure 7.8. Note also, in Figure 7.8 the provision for introducing heated ambient air to the sampling line.

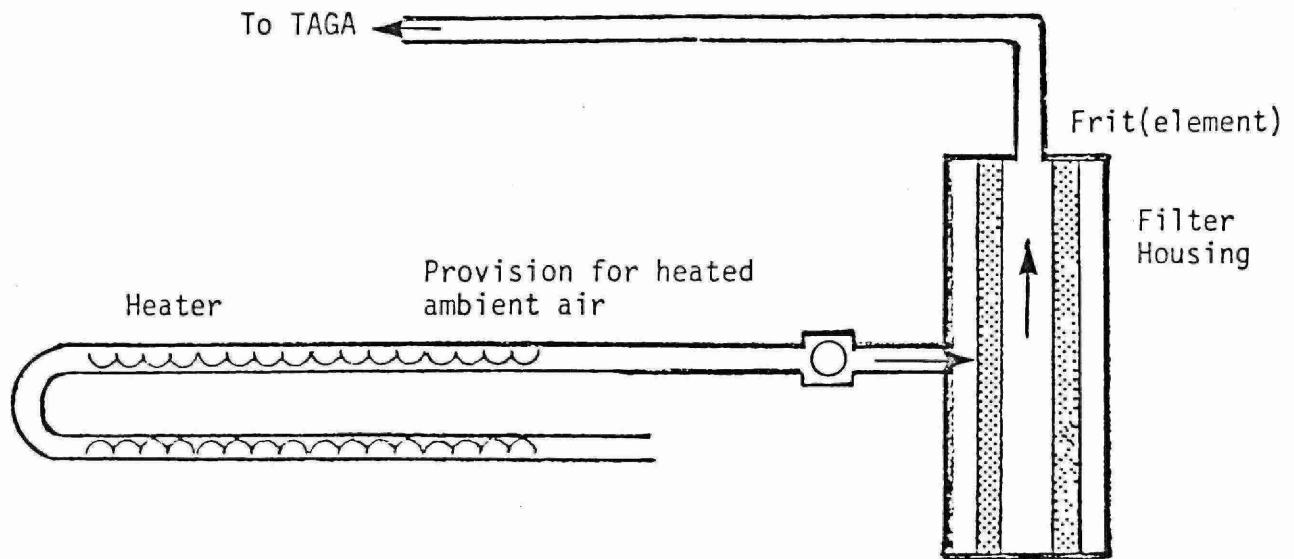
### Experimental Results and Data

For the initial studies of stack gas with the  $\frac{1}{2}$  ft<sup>2</sup> (46.5 cm<sup>2</sup>), 5-micron pore quartz filter, the sampling line was washed with dilute hydrochloric acid and rinsed thoroughly with water to remove dust and other potential interferences. The response of the TAGA<sup>TM</sup> 3000 was confirmed in cold ambient air, and after establishing a relatively constant 100% stack gas background, approximately 7000 ng/m<sup>3</sup> of total PCB was injected but the response to PCB was not significantly above the background (Table 7.2). The increase in the mono and di regions appear to be due to the fluctuating kiln conditions.

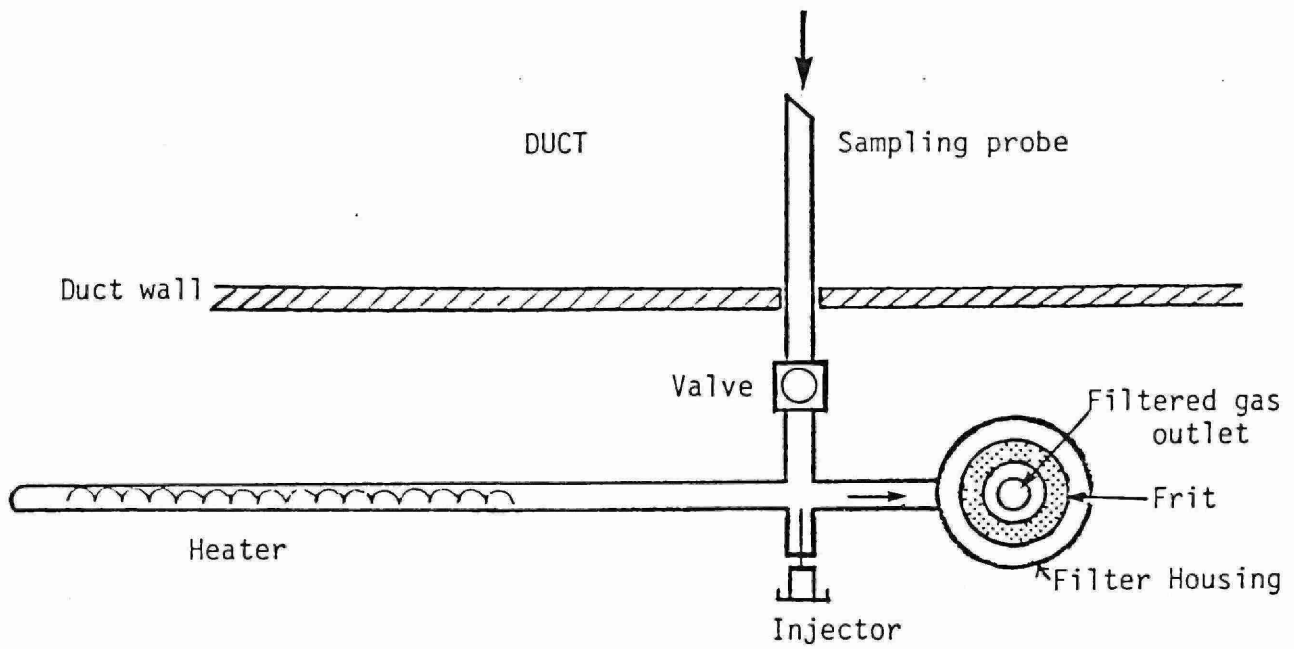


PHOTOS OF FRITTED QUARTZ FILTER HOLDER  
Figure 7.7

FIGURE 7.8 SCHEMATIC OF FRITTED QUARTZ FILTER INSTALLATION  
(Flanges Omitted)



(a) Side View



(b) Top View

TABLE 7.2

TAGA RESPONSES TO PCBs IN HEATED AIR  
AND 100% STACK GAS

SPECIES	MONO		DI		TRI		TETRA	
m/z	188	190	222	224	256	258	290	292
Heated Air, BKGD (ions) n=6	2214	2724	7197	5518	4083	3513	1668	1848
A PCB + Heated Air (ions) n=5	5739	5097	17057	12569	11231	9774	4882	5238
Response factor (ions/ng/m <sup>3</sup> )	6.3	4.3	26.3	18.9	13.7	11.8	4.7	5.0
Stack Gas, BKGD (ions) n=7	35004	36690	36690	93581	73018	32940	16318	17556
B Stack Gas + PCB (ions) n=5	42703	52176	99516	78955	36255	33296	16285	17078
Response Factor (ions/ngm <sup>3</sup> )	13.9	28.0	15.9	15.8	-1.5	0.7	-0.05	-0.7

A: Outdoor air passed through heated sampling line

B: 100% stack gas after condensation

Known amounts of PCBs were injected into the sampling line just upstream of the TAGA. The increase in the mono to di-regions are, most likely, due to the fluctuating kiln operating conditions.

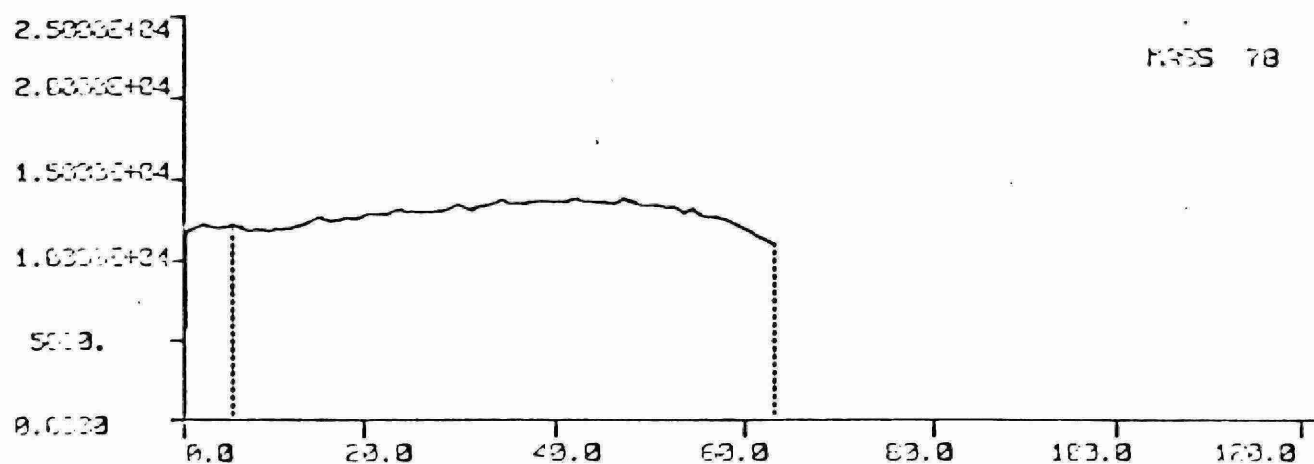
The probable causes of the reduced response to PCB in 100% stack gas were considered to be:

- (1) depletion of the CI reagent (benzene molecular ions) by,
  - (i) more rapid reaction with stack gas components than with PCBs.
  - (ii) disruption of the benzene concentration in the plenum chamber
- (2) adsorption efficiency changes related to the operation of the adsorber below atmospheric pressure.

#### Depletion of the CI reagent

The former problem was first studied by comparing the benzene ion signal during desorption of ambient air and stack gas samples. (Figures 7.9 and 7.10). Note the relatively massive depletion of benzene ion in the stack gas sample; thus it appeared that there was depletion of reactant ions by stack gas components. Attempts to identify these components consisted of scanning the positive and negative ion spectra during desorption and these spectral features will be discussed in Chapter 9. A further concern was the disturbance of the molecular benzene concentration during insertion of the probe into the desorb position; upon opening the nylon valve (See Figure 3.13) the lower pressure sampling line drew benzene vapor and prepurified air carrier from the ionization region, and in so doing, depletes the benzene ion signal. The benzene ion signal was found to require a substantial time period to recover to the levels measured prior to the insertion of the probe and the recovery time was independent of the depression of the sampling line. These data are listed in Figure 7.11.

A further study of the effects of benzene depletion involved the measurement of TAGA<sup>TM</sup> responses while allowing various times between inserting and heating the probe. Even after sufficient time (two minutes)



ADJUTANT AIR BY VAN

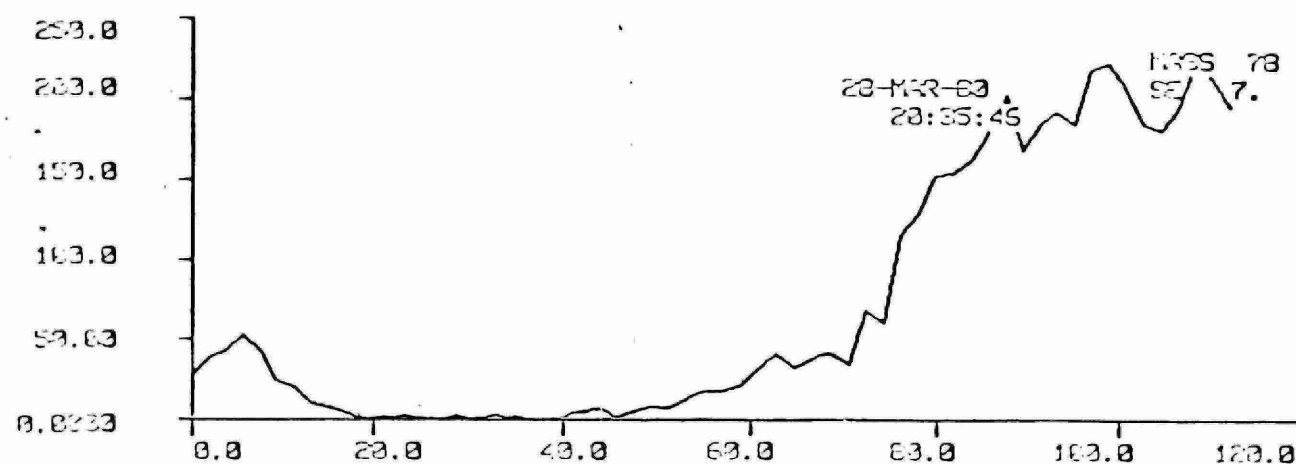
MDS	IGS	ERKION	CONC	RATIO
103	0851.	-1119.	0.0000000000*	
78	09427.	63419.	0.0	74.819
722	12513.	2524.	0.0	1.312
724	10497.	1119.	0.0	0.737
256	37015.	1234.	0.0000000000*	
723	12702.	-5073.	0.0	0.715
253	0402.	-9523.	0.0	0.476
252	5533.	-12234.	0.0	5.418

M1	187.03	R1	118.03	C1	0.00000
M2	78.703	R2	118.03	C2	0.00000
M3	221.03	R3	118.03	C3	0.00000
M4	223.03	R4	118.03	C4	0.00000
M5	255.03	R5	118.03	C5	0.00000
M6	257.03	R6	118.03	C6	0.00000
M7	259.03	R7	118.03	C7	0.00000
M8	261.03	R8	118.03	C8	0.00000

4-NOV-79	AS	18:27:15	DF	47.000	DI	-0.86000	L1	45.000	
SE	163.	AT	123.00	PR	0.00000	IN	650.00	L2	15.000
SY	23.	AF	4.5000	DS	60.000	RO	10.000	L3	15.000
OP	22.	OT	-43.450	TI	0.11667	MJ	-5000.0	L4	-240.00
PD	4.	PS	1.2500	ST	5.0000	EN	63.000	L5	-4.0000

TYPICAL BENZENE DESORPTION CURVE WITH NO STACK GAS

Figure 7.9



MSG	IONS	CONC	THREAT	OBDRAT
78	5.	5.	0.00	3462.00
103	17410.	17410.	0.00	0.00
222	27970.	27970.	0.65	0.78
224	21845.	21845.	0.65	0.00
225	2344.	2344.	0.93	0.93
228	2733.	2733.	0.93	0.00
229	1019.	1019.	1.33	1.00
232	1016.	1016.	1.33	0.00
324	453.	453.	1.63	0.59
326	283.	283.	1.63	0.00
333	653.	653.	0.31	1.00
352	705.	705.	0.81	0.00

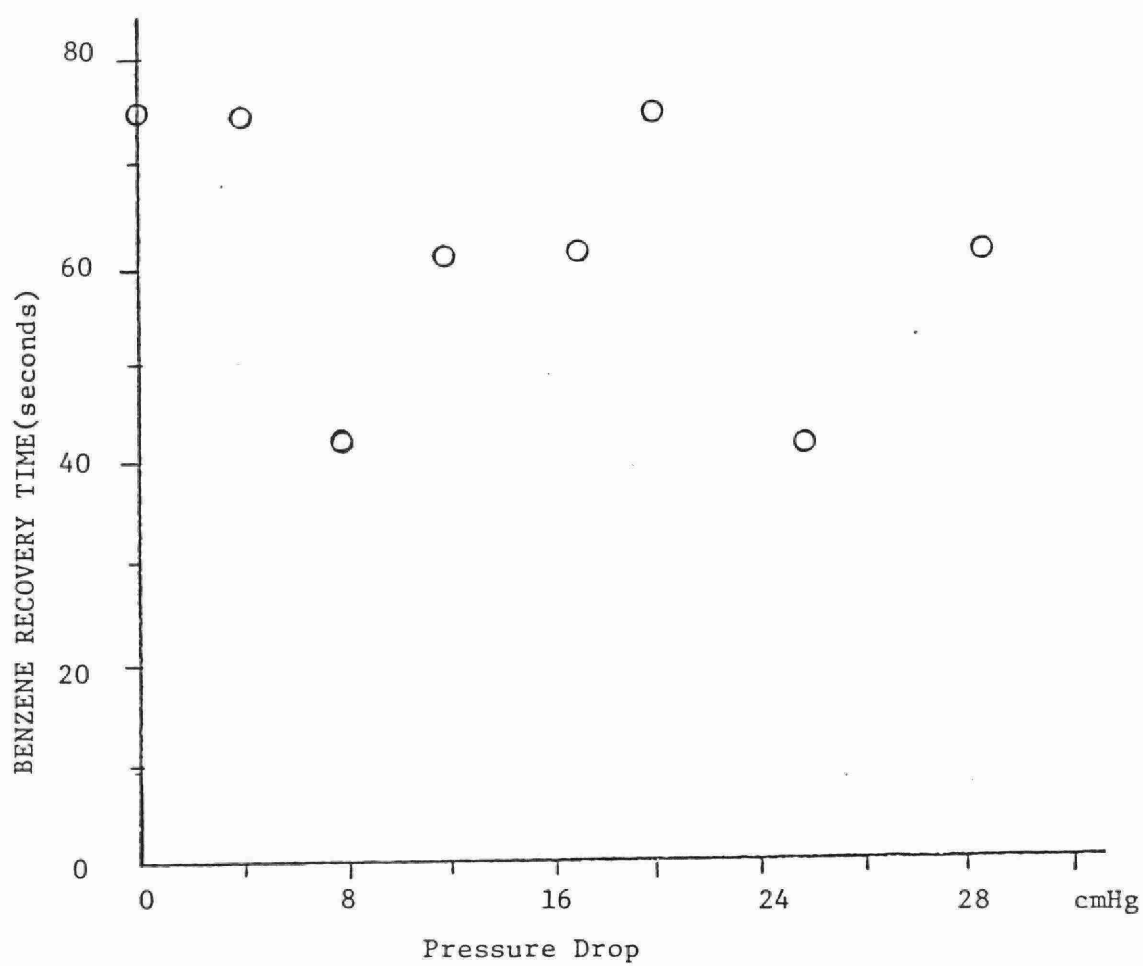
100% STACK GAS DILUTED WITH HEATED AMBIENT AIR

DEPLETION OF BENZENE REAGENT IONS CAUSED BY STACK GAS  
(Concentrated)

Figure 7.10



FIGURE 7.11 BENZENE ION RECOVERY TIME vs PRESSURE DROP



for complete recovery of benzene, the response was not significantly different from that measured when no recovery time was allowed. Thus the disruption of the benzene by exposure to the depressed sampling train did not appear to be responsible for the reduced sensitivity to PCBs.

#### The effects of line pressure

The effects of line pressure on the inlet system were examined by creating a pressure depression by constriction, and drawing the heated ambient air sample through the sampling line. Plots of ion signal vs line pressure revealed a strong direct dependence of signal on pressure drop. A representative plot is shown in Figure 7.12. The decrease in pressure was considered to cause desorption of interfering compounds from the glass tubing, thus increasing the concentration of these undesirable components.

The measurement of the sample flow will also be affected by decreased pressure since the pressure drop across the orifice ( $\Delta P$ ) is related to the flow ( $q$ ) by an expression involving the density of the gas.

$$q = \frac{2.8 \times 10^{-2} \Delta P^{1/2}}{\sqrt{\delta}} \quad \text{Where } \delta = \text{Gas Density (g/ml)}$$

(See Appendix 2 of Reference 8 for details)

Therefore a decrease in the density results in an increase in the flow for the same  $\Delta P$ . This factor would contribute to the background intensities since, during the measurements a constant  $\Delta P$  was maintained as the depression increased. This factor accounts for only 10-15% of the ca. 50% increase in background signals resulting from a pressure change of 760 mm Hg to 660 Hg.

#### Transmission of PCBs through the filter

A further constraint on the filter element was that it would not hamper the transmission of PCBs. In a study with 100% stack gas flowing (1.7 l/sec) through the heated frit and line ( $120^\circ$ ),  $1.6 \text{ ug/m}^3$  of total PCBs was injected for one hour at Injection Port 1 just upstream of the

# ION SIGNAL OF OUTDOOR AIR VS LINE PRESSURE

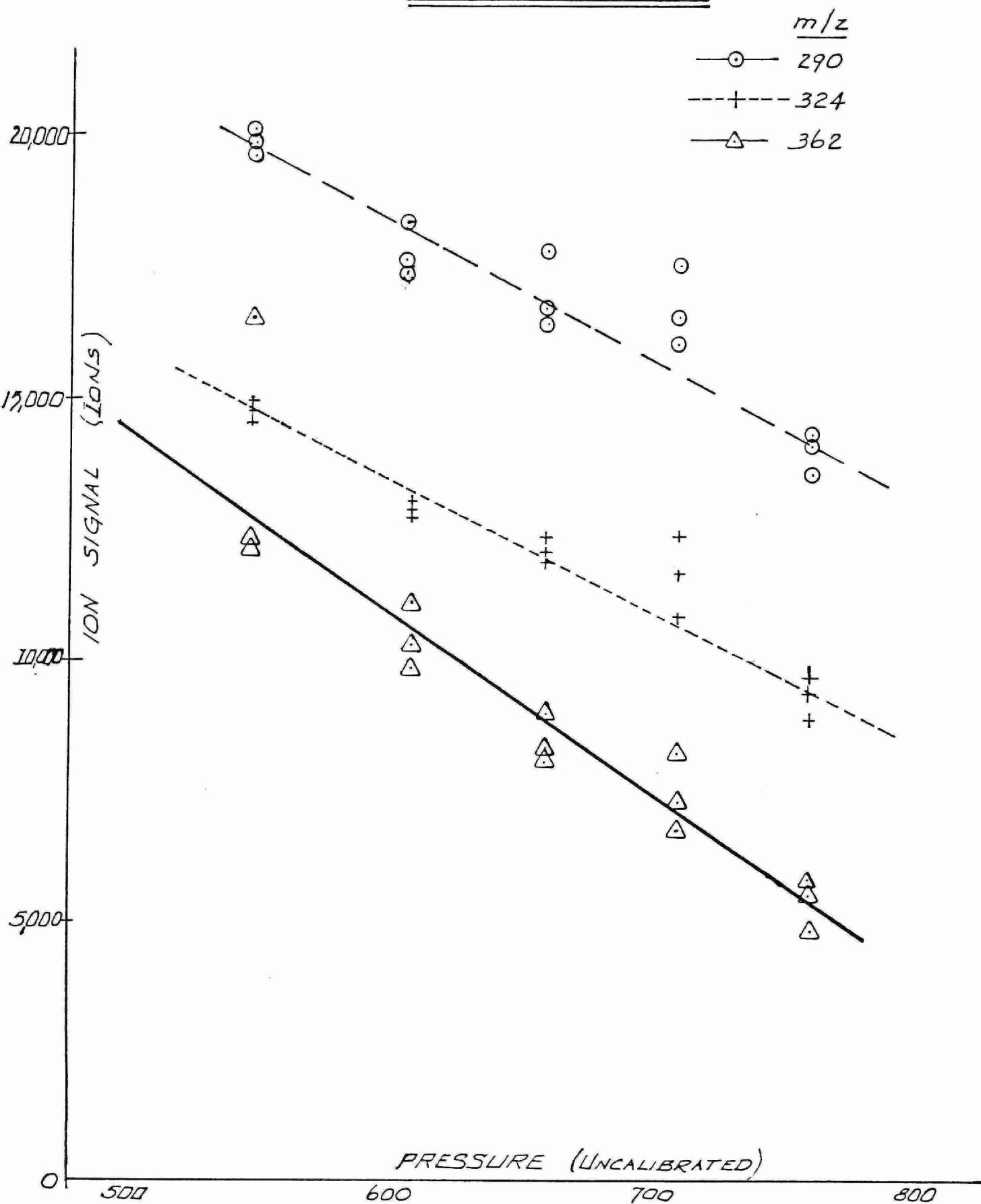


Figure 7.12

quartz filter (Figure 7.3). Subsequent extraction of the dust and frit by the Laboratory Services Branch showed that less than 1% of the injected PCB had been trapped. These results are summarized in Table 7.2a.

TABLE 7.2a

RETENTION OF INJECTED PCBs  
BY 10-MICRON QUARTZ FILTER

- Analysis done by the Pesticides Section of MOE -

PCB SPECIES	MONO	DI	TRI	TETRA	PENTA	HEXA
Amount Injected (ng)	14440	9786	13802	17851	14917	33502
Amount Recovered from Condensate (ng)	42	736	2056	2712	2911	5021
% Retention in condensate	0.3	8	15	15	20	15
Amount Recovered from Dust (ng)	198	1.7	ND	63	11	ND
% Retention in Dust	1.4	0.02	ND	0.04	0.07	ND
Amount Recovered from Element (ng)	96	27	64	65	69	22
% Retention in Element	0.7	0.3	0.4	0.4	0.5	0.07

PCBs were injected into 100% stack gas upstream of a 10 micron pore quartz filter (464.5 cm<sup>2</sup> surface area) which had been cleaned by an ultrasonic bath and dried. The duct was mechanically scraped and extracted with hexane 3-times. All the extracts were combined for GLC analysis.

In a further attempt to extend further the useful lifetime of the quartz frit a wrapping of fibreglass filter paper was used; the filter paper collected substantial amounts of dust and did not cause further restrictions to the gas flow.

Fritted quartz elements with 5  $\mu$  and 25  $\mu$  pore sizes were also acquired, however the 5  $\mu$  frit required excessive pressure depression (28 cmHg) to reach 1.7 l/sec, and the 25  $\mu$  frit was considered to be too coarse to filter properly.

#### 7.1.4 Cyclone Precipitator.

The sensitivity threshold of the TAGA<sup>TM</sup>3000 is very dependent on the background ion signal, that is, as the background rises so does the detectability limit. Since the background ion signals appeared to be strongly dependent on pressure depression, the cyclone separator offered the potential to minimize depression (and to maximize TAGA sensitivity.

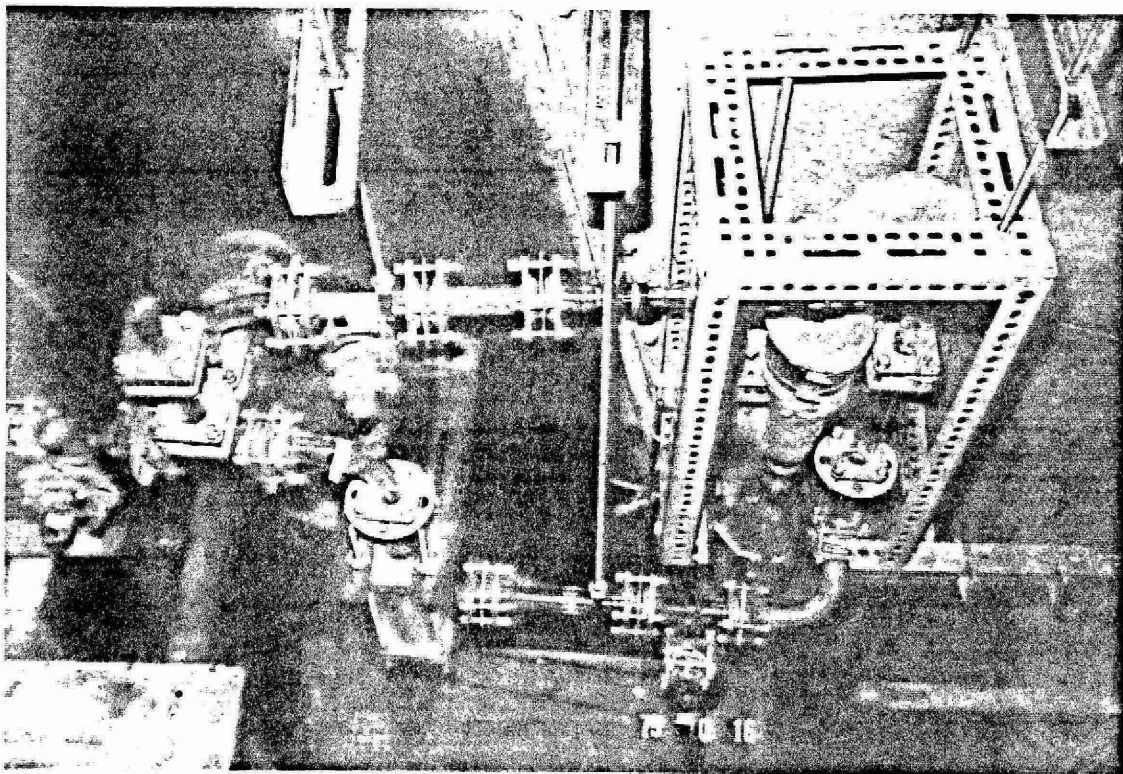
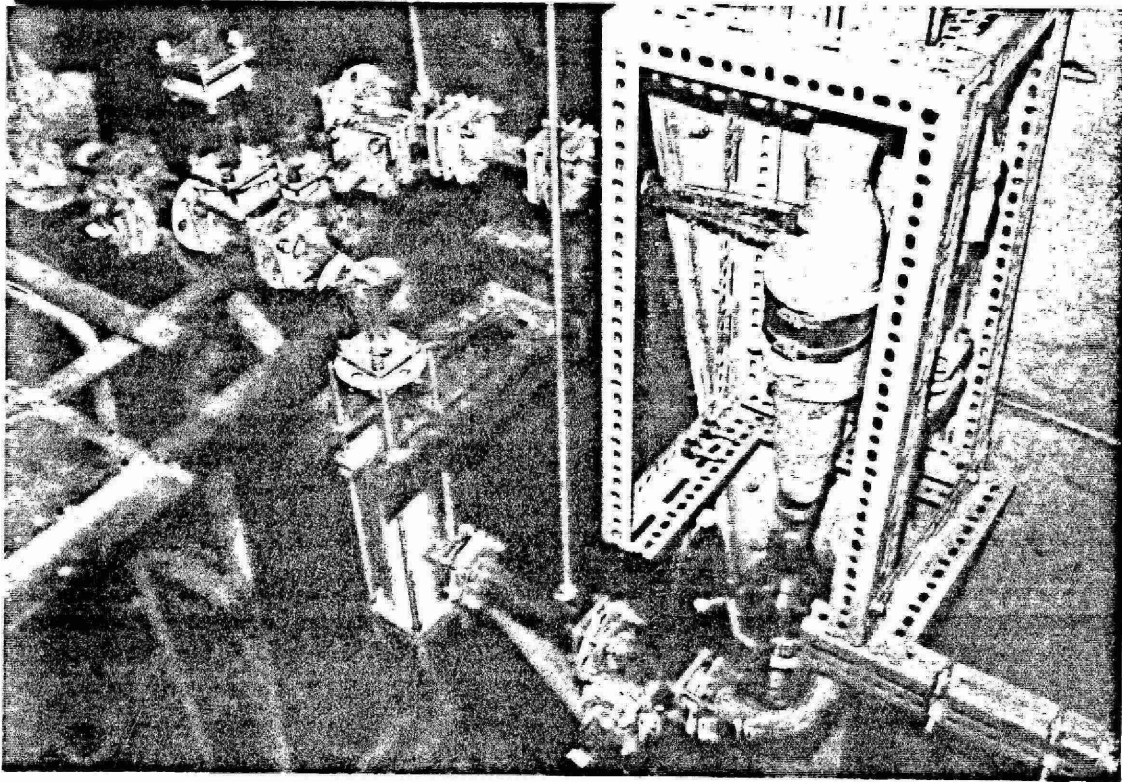
The glass cyclone is described in detail in Report #78-01 submitted by N.G.H. Guilford of the Ontario Research Foundation to Sciex Inc. on January 23, 1978 (Ref. 14). The cyclone was installed as shown photographically in Figure 7.13. The dimensions of the cyclone are shown in Figure 7.14.

### Results and Discussion

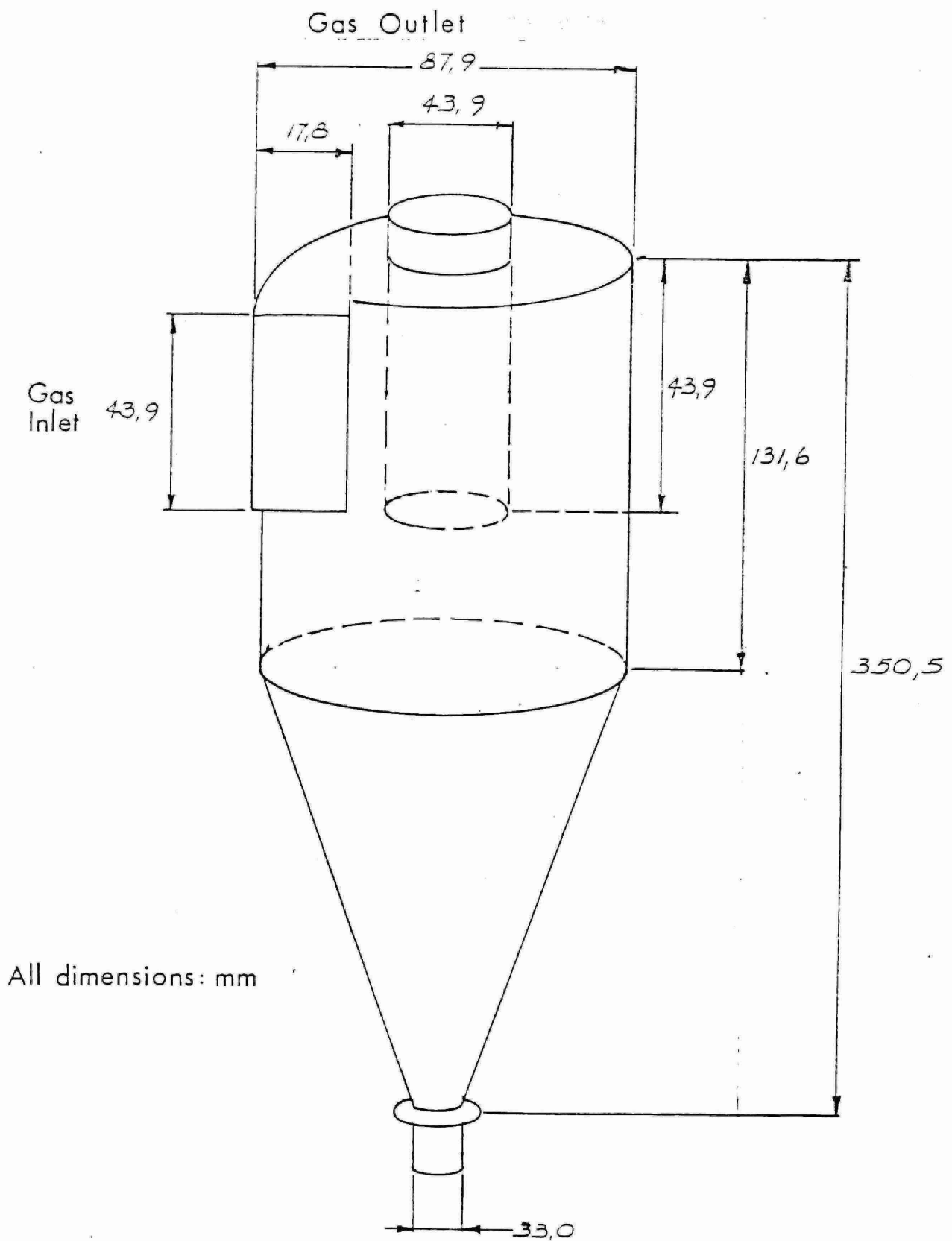
Attempts to achieve the 15 l/sec flowrate required for efficient filtration were fruitless. Ambient air was drawn through the cyclone system and the maximum achievable flowrate was 13 l/sec with 50 cmHg. of pressure depression. The sampling line and cyclone were not readily compatible.

#### 7.2 Modifications to the PCB Front End

The first studies with glass wool filters demonstrated the need for improvements to the sealing of the sample integrator system, to prevent air from being drawn in from the van atmosphere. Sketches of the currently used model to seal the adsorber system are shown in figures 7.15 and 7.16. O-Rings #2, #4 and #5 are intended to prevent van air from



PHOTOS OF GLASS CYCLONE SEPARATOR  
Figure 7.13



### CYCLONE DIMENSIONS

Figure 7.14



seeping into the sampling region during adsorption, (Fig. 7.15) and #3 is used to prevent CI reagent gases from being drawn from the plenum chamber during desorption (Fig. 7.16). This system of O rings was found to remain sealed to considerable line depression.

### 7.3 Dilution of Stack Gas

Earlier experiments (section 7.1.3) showed that components of stack gas interfered with sensitive detection of PCBs in the source, because in 100% stack effluent there were substantial background ion signals at the m/z values of interest to PCBs. In order to reduce the background ion signals dilution of the sample was necessary. Initial experiments with the dilution technique entailed the use of the apparatus shown in Figure 7.17. The flow of the ambient air diluent measured with the magnehelic (M2) gauge and the stack sampling line was opened to make up the remainder of the 1.7 l/sec flow.

When PCBs were injected just upstream of the TAGA<sup>TM</sup> 3000 unit (IP4), good signals were obtained. However, the same solution did not produce significant responses when injected at IP1 and IP2. Then, the solution was injected at immediately downstream of the water vessel (IP 3 in Figure 7.17) to isolate the source of the PCB retention. Table 7.3 indicates PCB transmission in the range of 25-60%. Because of the very long line (approximately 11 m) between the water vessel and the TAGA<sup>TM</sup> unit and the relatively slow flow rate (0.2 l/s), the PCBs injected at IP 3 tend to deposit on the line walls. There were a number of elbows and Tee pieces which might have contributed to the retention of the PCBs. Cold weather in the winter also created problems in maintaining the sampling line hot. The HE-6 heat exchanger cooled down the stack gas too much and removed the PCBs from the stack gas, when PCBs were added at IP1 or IP2.

### 7.4 Final Sampling System Design

For these reasons dilution was made just downstream of the duct probe with heated ambient air, as shown in Figure 7.18. In this configuration the heated ambient air-stack gas was brought down to the MOE van at a relatively high flow rate (1.7 l/s) at 120°C and above. The temperature of this stack gas/heated ambient air mixture was reduced to 50°C with an 80 cm long heat exchanger installed just upstream of IP

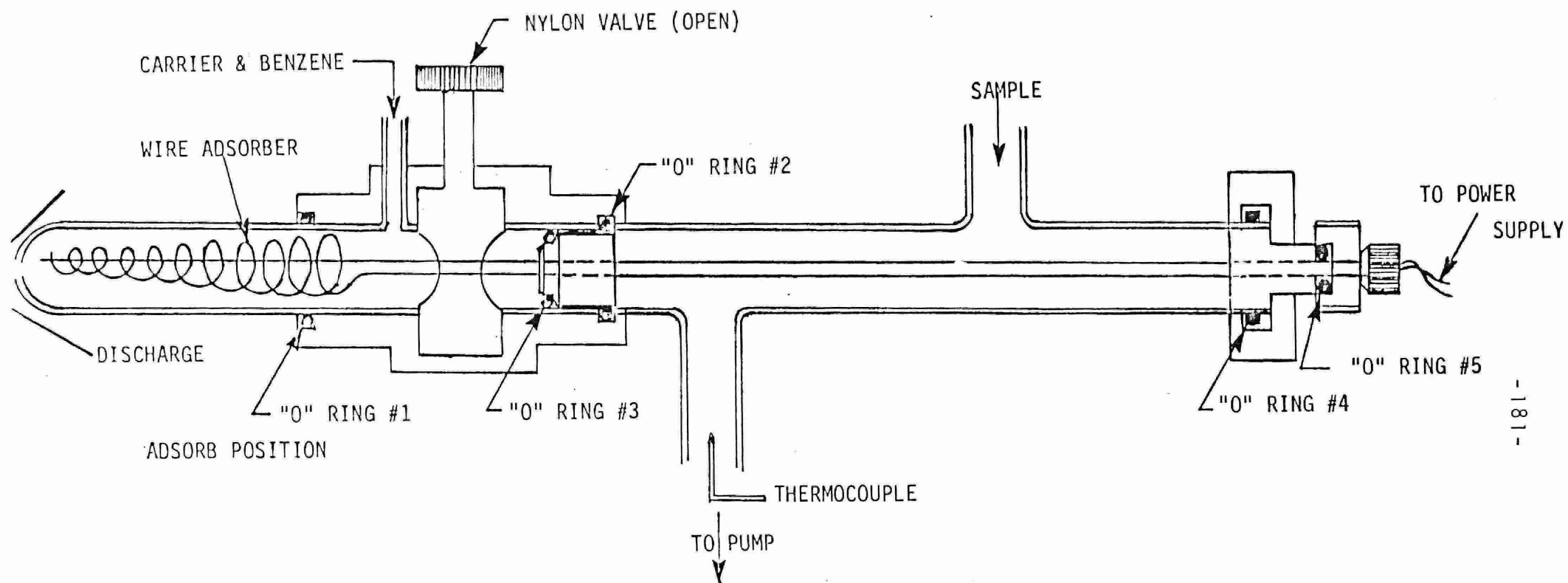


FIGURE 7.15 FINAL ATTEMPT TO SEAL ADSORBER SYSTEM

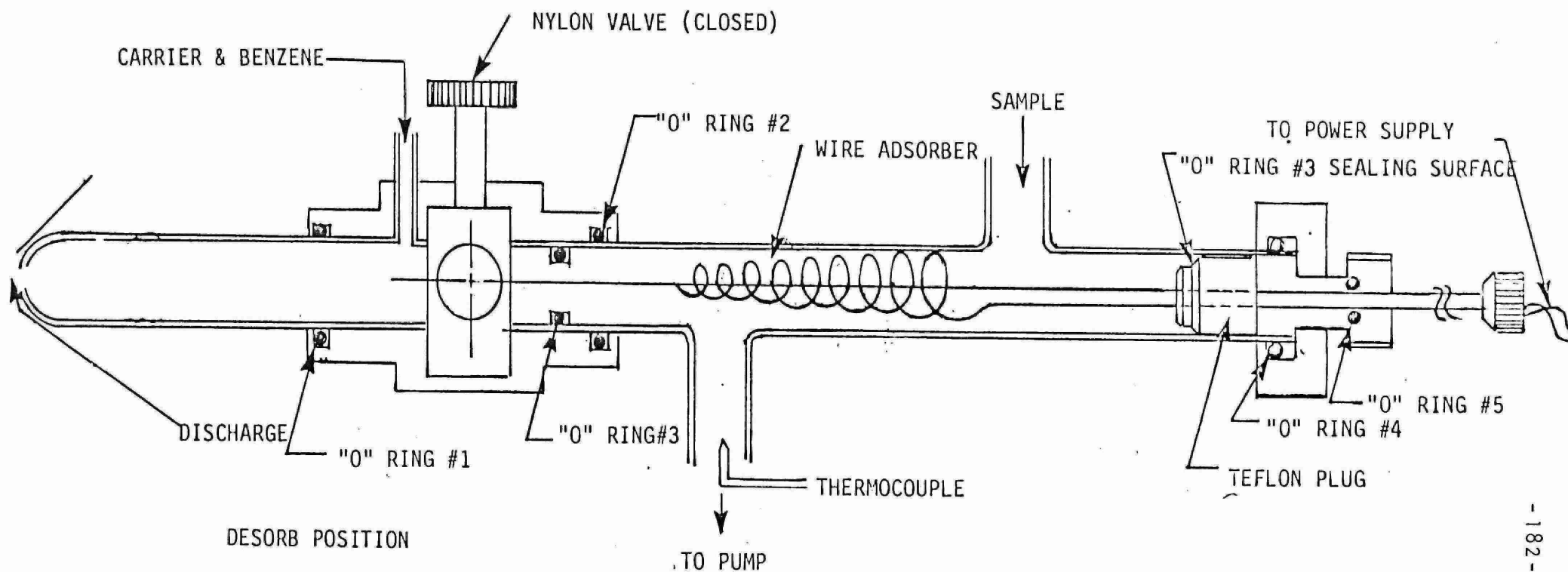


FIGURE 7.16 FINAL ATTEMPT TO SEAL ADSORBER SYSTEM

TABLE 7.3

PCB TRANSMISSION FROM WATER VESSEL TO TAGA

SPECIES	MONO	DI	TRI	TETRA
Concentration (ug/m <sup>3</sup> )	2.251	1.526	2.151	2.783
m/z	188	222 224	256 258	290 292
Net Response IP 4	3137	4680 3080	4514 3959	1544 1854
Net Response IP 3	1113	1876 1302	2654 1848	453 475
% Transmission	35.5	40.1 42.3	58.8 46.7	29.3 25.3

These net responses are averages of 4-8 measurements.

IP 3: Injection port just upstream of the TAGA<sup>TM</sup> unit

IP 4: Injection port just downstream of the water vessel.

See Figure 7.17

4 (injector just upstream of the PCB wire integrator). Thermostatically controlled water was circulated through this heat exchanger to adjust the temperature of the stack gas-air mixture. This final system gave very satisfactory line characteristics as described in the next chapter.

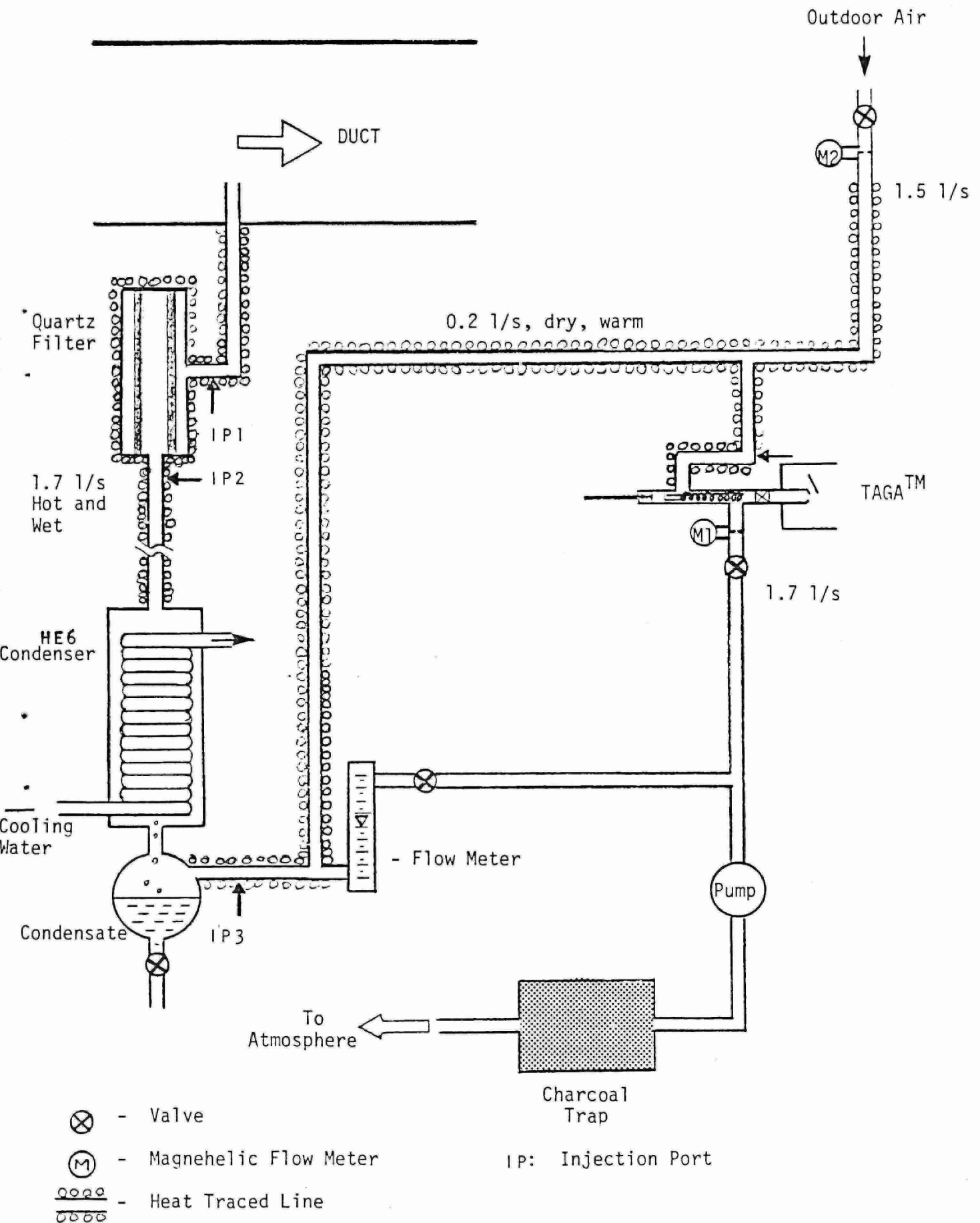
The schematic (Fig. 7.18) shows that the stack gas sample flow is diluted by a measured flow of heated ambient air. This large dilution (typically between 4:1 and 10:1) has been found to be an extremely effective and simple solution to several problems.

First, dilution lowers the dew point of the diluted sample to about 30°C, so that the sample gas can be allowed to cool to 50°C just before reaching the TAGA<sup>TM</sup> wire adsorber without fear of condensation occurring. This is a great simplification because it eliminates the requirement for a water condenser in the line, which in practice proved difficult to operate.

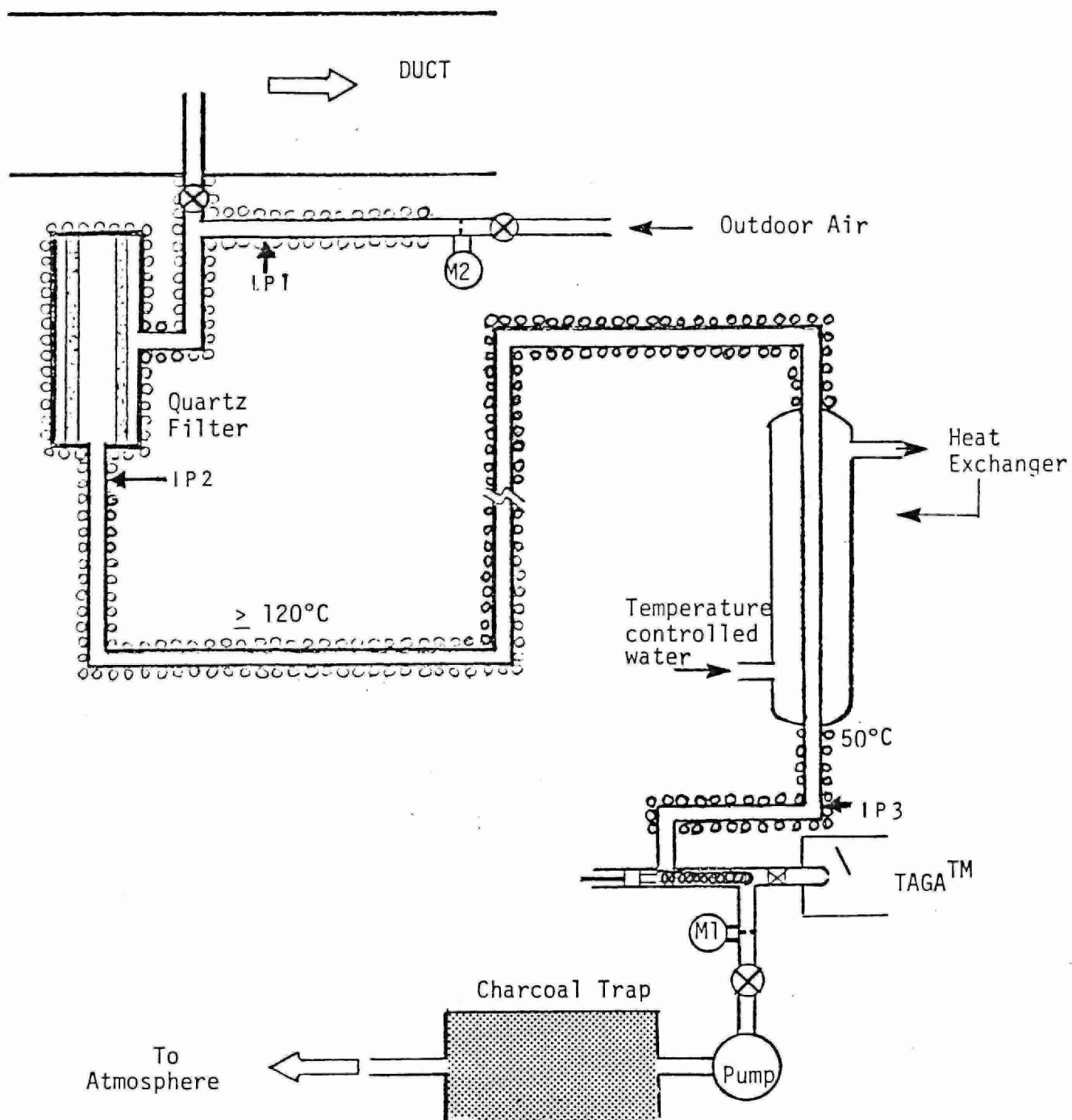
A second improvement relates to filter operations. As indicated in Figure 7.18, the hot diluted stack gas is passed through a 10/micron fritted quartz cylinder of about 1 ft<sup>2</sup> (0.093m<sup>2</sup>) surface area. Dilution allows the total line flow rate to be kept high (1.7 litres/sec) for rapid response while keeping the pressure drop and dust loading low.

This filter which can be readily replaced has been operated for many hours without showing any increase in pressure drop as a result of dust build-up. It is totally effective in eliminating the dust build-up problem on the glass walls or on the adsorber surface at the TAGA<sup>TM</sup> 3000.

PCBs present in the stack have been seen dominantly in the gas phase rather than adsorbed on the cement dust because of the elevated temperature (Ref. 4). The design concept for the sampling line therefore was aimed at trapping the dust at elevated temperatures, where no significant loss of PCBs from the sample would occur. To test this hypothesis, PCBs were injected at IPl and both the loading of cement dust and the filter element were then analyzed for PCB content by solvent extraction and conventional analysis carried out at the Ministry of the Environment Laboratory Services Branch.



DILUTION EXPERIMENT (1)  
FIGURE 7.17



(M) Magnehelic Flowmeter

(X) Valve

Heat Traced Line

IP Injection Port

DILUTION EXPERIMENT (11)

FIGURE 7.18

The results given in Table 7.2 indicated that, on the average, less than 1% of PCBs are adsorbed on the hot filter. Since this is an insignificant error in terms of the Test Protocol requirements (Ref. 5), this final filter design is felt to be a successful solution to remove particulates and these results prove conclusively that no PCBs are trapped between point IP 1 and IP 2 and that PCBs exist in their vapor form.

A third improvement resulting from dilution relates to interfering compounds in the stack gas which complicate the detection of PCBs by the TAGA<sup>TM</sup>. Initial testing showed that undiluted stack gas contained compounds which produced "background signals" at the PCB mass peaks and which also reacted with the chemical ionization reagent added just upstream of the TAGA<sup>TM</sup> (see Figures 7.9 and 7.10). Since the TAGA<sup>TM</sup> cannot detect PCBs until the added reagent has reacted with the PCBs to ionize them, the composition of the sample gas stream had to be altered so that the reagent would survive. By diluting the stack gas, the interference was reduced substantially and the TAGA's sensitivity toward PCB was improved.

Since the sample was diluted a correction factor must be made to convert the concentration measured by the TAGA<sup>TM</sup> back to the concentration actually present in the exhaust duct being sampled. The correction is made by measuring flow rates and pressure in the sampling line and performing the calculations when the measurements are made. As an example of how the calculations work, suppose that the total concentration of PCBs in the stack gas flowing through the exhaust duct is  $2.0 \text{ ug/m}^3$ , and suppose that 1 part of sampled stack gas is diluted to 9 parts of air. In this case, the TAGA<sup>TM</sup> would actually detect a total concentration of approximately  $0.2 \text{ ug/m}^3$ , but when this signal was measured, the dilution would be accounted for and the number reported to authorities would be " $2.0 \text{ ug/m}^3$  of total PCBs in the stack gas". The detectabilities cited in the following chapter of this report have been corrected in the manner discussed above.

Figure 7.19 is a 3-dimensional schematic of the final sampling line. Please note that injection ports, valves and thermocouples are numbered here in a reverse order from those in Figures 7.17 and 7.18.



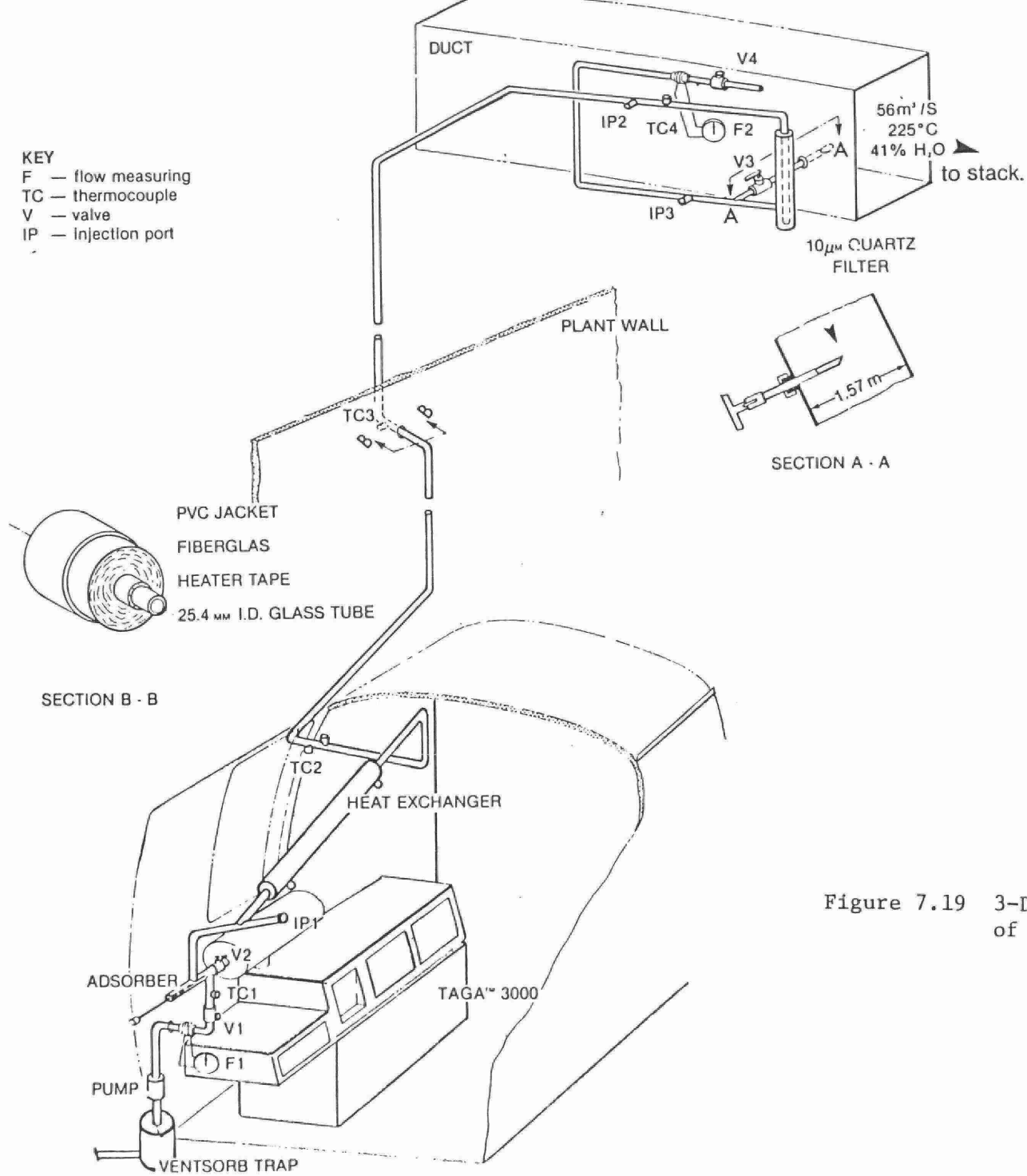


Figure 7.19 3-Dimensional Schematic of Final Sampling Line

## 8.0 EXPERIMENTAL RESULTS

Using the final workable sampling line system described in Section 7.4 a number of experiments were undertaken to study the behavior of PCBs in the sampling line. These experiments include (a) the transmission of PCBs across the 10 u quartz filter assembly, (b) time response test of the total system, (c) total system response to individual PCB species, and (d) the system's response to a mixture of PCBs introduced through the three injections ports, i.e., PCB budget along the sampling line. These experiments will be discussed in this order.

### 8.1 PCB Transmission Across the Quartz Filter

The sampling line as described in the preceding sections, was operated at a temperature of 120°C and above, and thus the trapped particulate matter on the 10 micron (918 cm<sup>2</sup>) quartz filter and housing was kept at this elevated temperature to minimize any retention of PCBs. It has been shown in Table 7.2 that PCBs injected upstream of the filter IP 1 in Figure 7.18 were not retained by the dust loading or filter assembly to a significant degree. The analysis was done by solvent extraction and gas chromatographic analysis; but in view of the nature of the overall performance of the TAGA<sup>TM</sup> and the sampling system this conclusion was confirmed by the use of the MOE TAGA<sup>TM</sup> itself.

Using this same stack sampling and gas dilution system as in Figure 7.18, the TAGA system was stabilized by establishing steady background readings for the mass spectral region from mono- to hexa-chlorobiphenyl species. Standard solution, #2 described in Table 3.6 containing known amounts of the PCB species was injected downstream of the quartz filter (IP 2). The system was then returned to background monitoring to ensure that no residual PCBs were left in the sampling line. The standard solution was then identically injected upstream of the quartz filter (IP 1). If any PCBs were retained by the filter assembly or dust loading, the response of the TAGA system would be lower for injections at IP 1 than injections at IP 2.

Table 8.1 lists the total responses obtained by injecting

Table 8.1

Transmission of PCBs Across Quartz Filter. The parameter m/z, x and n denote the mass to charge ratio, the average response and number of observations, respectively. The s parameters are the statistical standard deviations.

Species	m/z	Equivalent Concentration (ug/m <sup>3</sup> )	Response at IP 2 Downstream of Filter (ions)		Response at IP 1 Upstream of Filter (ions)		Component Background (ions)		Overall (s')	Transmission (%)*
			x (n = 3)	s <sub>1</sub>	x(n=5)	s <sub>2</sub>	x(n=8)	s <sub>3</sub>		
Mono	188	10.2	5562	520	6088	1269	1441	154	808	109.4 + 14.5 (%)
Di	222	6.9	4414	127	4822	614	1398	85	379	109.2 + 8.6
	224	6.9	2953	62	3207	268	1172	101	180	109.2 + 6.0
Tri	256	9.8	5266	91	5036	535	1717	263	378	95.6 + 7.2
	258	9.8	4692	131	4539	574	1434	184	491	96.7 + 10.5
Tetra	290	12.6	825	82	876	92	238	72	87	106.2 + 10.5
	292	12.6	1091	113	1143	151	323	108	133	104.8 + 12.1
Penta	324	10.5	1440	218	1435	139	648	189	195	99.7 + 13.5
	326	10.5	2065	302	2109	254	826	299	308	102.1 + 14.9
Hexa	360	23.7	1445	114	1355	76	633	141	128	93.8 + 8.9
	362	23.7	1501	153	1366	69	634	155	143	91.0 + 9.5

\* Obtained by

$$100(\%) - \frac{\text{Response (IP 2)} - \text{Response (IP 1)}}{\text{Response (IP 2)}} \times 100 (\%) =$$

$$\text{Range} = \frac{s'}{\text{Response (IP 2)}} \times 100 (\%)$$

the PCBs at IP 1, IP 2 and composite background readings taken before, between and after the injections. The standard deviations,  $S_1$ ,  $S_2$ , and  $S_3$ , are the statistical measures of variability that apply to the responses. The  $S$  for each PCB was calculated by the Pooled Variance Method, and indicates the degree of overall standard deviation. The last column in Table 8.1 shows that for any PCB species injected, the analytical results compared well to that obtained earlier by the Ministry's Laboratory Services Branch.

## 8.2 Time Response Test of the Total System

In order to examine wall effects of the total sampling system, Standard Solution #2 was injected at IP 1 (upstream of the quartz filter). Figure 8.1 indicates a very rapid signal rise when the PCBs were added to the line, and a sharp decay of the signal when injections were halted. The plot of the TAGA<sup>TM</sup> response against time demonstrates that wall effects downstream of IP 1 in the proximity of the duct probe have been virtually eliminated.

## 8.3 Total System Response to PCBs

The total system's response to PCBs was determined by injecting various known amounts of Standard Solution #2 (See Table 3.6) at IP 1 (injection port upstream of the quartz filter, See Figure 7.18). Injections were made under normal kiln operating conditions while drawing 0.2 litre per second of the stack gas through the line and diluting with heated (100-130°C) ambient air drawn from upstream of the quartz filter. The total flow was 1.7 l/s, the stack gas comprising 11.6% of the gas mixture. These experiments were conducted to test and validate the total system's response including the quartz filter and cement dust loading.

The experimental results have been analyzed using a statistical computer program, "The Least-Squares Method of Curve Fitting", where the TAGA<sup>TM</sup> response and the concentration of added PCBs are fitted to a mathematical equation representing the structural relationship between the two variables. This procedure has been described in detail in Chapter 4.

Tables 8.2, 8.3, 8.4, 8.5, 8.6 and 8.7 show the TAGA's total response to the PCB injection into the diluted stack gas upstream of the filter (IP 1). The responses are expressed in number of ions and the concentration of injected PCBs in micrograms per cubic meter of the stack gas. The slope is the total system's sensitivity in terms of (ions)/(ug/m<sup>3</sup>). The intercept indicates the total system's response by statistics when no PCBs are added. The correlation coefficient (CORR.COEFF.) is a measure of the linearity between the total system's response and the PCB concentrations (1.000 being a perfectly linear response).

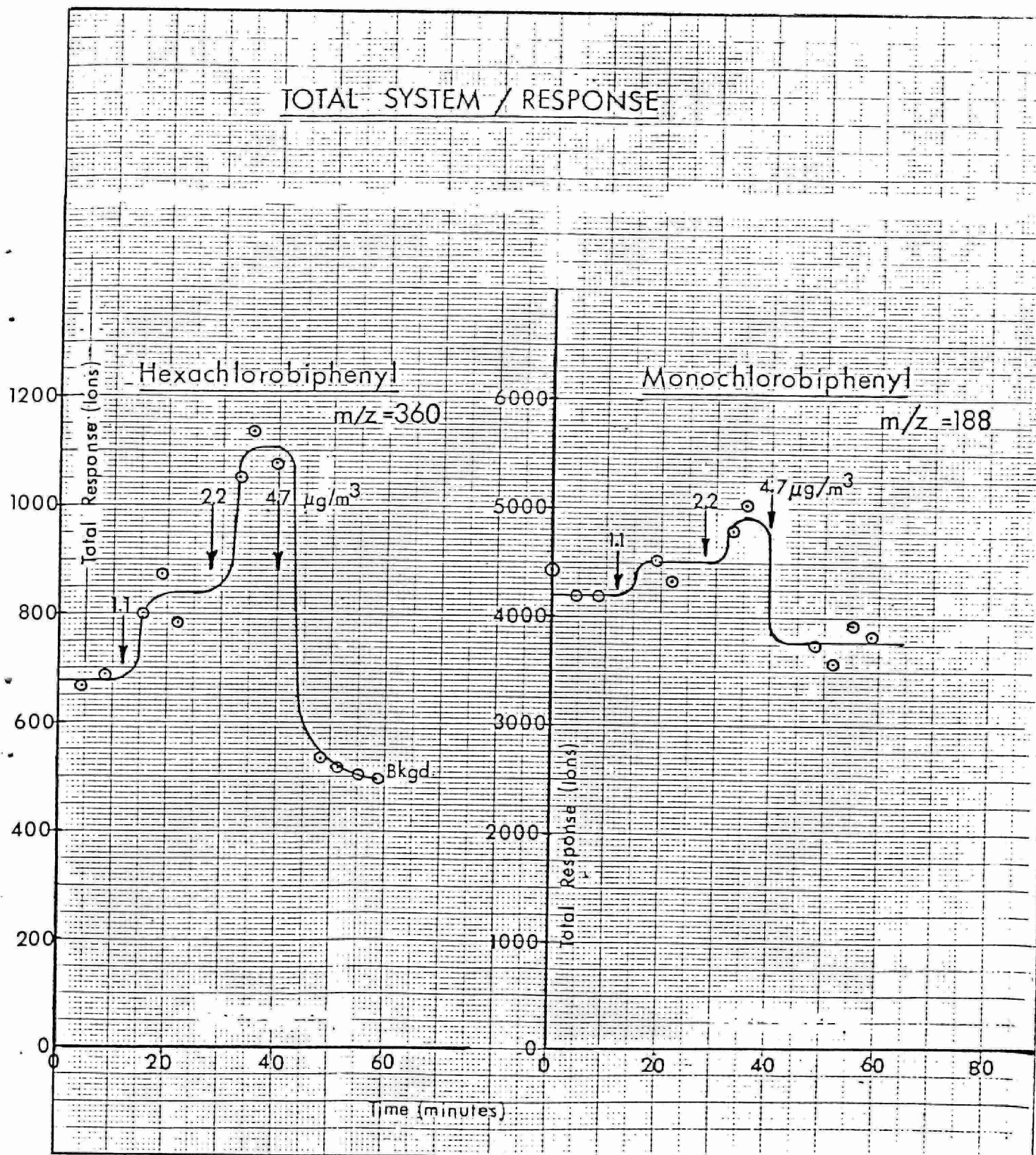


Figure 8.1

TABLE 8.2

MONOCHLOROBIPHENYL ADDED TO 12% STACK GAS UPSTREAM OF QUARTZ FILTER  
TOTAL RESPONSE VS CONCENTRATION

ROW	1 (188)	2 (ug/m <sup>3</sup> )
1	3820	0
2	3927	0
3	3570	0
4	3747	0
5	4625	4.763
6	5015	4.763
7	4774	4.763
8	6363	1.201
9	5769	10.201
10	6053	10.201
11	7607	19.406
12	8077	19.406
13	7904	19.406
14	4195	1.082
15	4199	1.082
16	4424	1.082
17	4312	2.217
18	4537	2.217
19	4388	2.217

For column 1 versus column 2

Slope 192.916

Intercept 4065.33

Corr. Coef 0.927961

3s Detection Limit  
31.0 ions 2.335 ng/m<sup>3</sup>

TABLE 8.3

DICHLOROBIPHENYL ADDED TO 12% STACK GAS UPSTREAM OF QUARTZ FILTER

TOTAL RESPONSE VS CONCENTRATION DICHLOROBIPHENYL

ROW	1 (222)	2 (224)	3 (ug/m <sup>3</sup> )
1	3075 ions	2685 ions	0
2	3310	2664	0
3	3213	2588	0
4	3566	2830	0
5	3804	2946	3.228
6	4185	3278	3.228
7	3953	3105	3.228
8	4452	3451	6.914
9	4547	3903	6.914
10	4719	3706	6.914
11	5900	4388	13.151
12	5976	4335	13.151
13	5639	4178	13.151

For column 1 versus column 2

Slope 1.4959  
 Intercept -735.863  
 Corr. Coef 0.980351

For column 1 versus column 3

Slope 191.558  
 Intercept 3304.09  
 Corr. Coef 0.986458

For column 2 versus column 3

Slope 124.015  
 Intercept 2722.38  
 Corr. Coef 0.974491

M/Z	3s	Detection Limit
222	622	3.247 ug/m <sup>3</sup>
224	303	2.443 ug/m <sup>3</sup>



TABLE 8.4

TRICHLOROBIPHENYL ADDED TO 12% STACK GAS UPSTREAM OF QUARTZ FILTER

TOTAL RESPONSE VS CONCENTRATION			
ROW	1 (256)	2 (258)	3 (ug/m <sup>3</sup> )
1	1357	1239	0
2	1387	1293	0
3	1340	1296	0
4	1337	1317	0
5	2302	2096	4.553
6	2319	2158	4.553
7	2197	2071	4.553
8	3083	2837	9.751
9	3011	2763	9.751
10	2958	2875	9.751
11	4418	4263	18.549
12	4704	4462	18.549
13	5038	4639	18.549
14	1765	1626	1.033
15	1637	1626	1.033
16	1661	1589	1.033
17	1840	1719	2.119
18	1877	1737	2.119
19	1808	1657	2.119

For column 1 versus column 2

Slope 1.06169  
 Intercept 6.96893  
 Corr. Coef 0.998601

For column 1 versus column 3

Slope 175.353  
 Intercept 1426.22  
 Corr. Coef 0.993374

For column 2 versus column 3

Slope 165.324  
 Intercept 1335.87  
 Corr. Coef 0.99573

M/Z	3s	Detection Limit
256	68.8	0.392 ug/m <sup>3</sup>
258	99.8	0.604 ug/m <sup>3</sup>

TABLE 8.5

TETRACHLOROBIPHENYL ADDED TO 12% STACK GAS UPSTREAM OF QUARTZ FILTER

TOTAL RESPONSE VS CONCENTRATION			
ROW	1 (290)	2 (292)	3 (ug/m <sup>3</sup> )
1	121	136	0
2	150	181	0
3	145	187	0
4	162	181	0
5	390	475	5.888
6	363	442	5.888
7	364	492	5.888
8	551	648	12.611
9	455	554	12.611
10	481	645	12.611
11	871	1018	23.99
12	899	1171	23.99
13	993	1226	23.99
14	224	266	1.337
15	205	238	1.337
16	201	243	1.337
17	276	291	2.74
18	256	312	2.74
19	266	304	2.74

For column 1 versus column 2

Slope 0.792047  
 Intercept 12.4553  
 Corr. Coef 0.996079

For column 1 versus 3

Slope 30.9015  
 Intercept 160.848  
 Corr. Coef 0.988136

For column 2 versus column 3

Slope 38.7887  
 Intercept 189.016  
 Corr. Coef 0.986276

M/Z	3s	Detection Limit
290	51.6	1.671 ug/m <sup>3</sup>
292	71.0	1.831 ug/m <sup>3</sup>

TABLE 8.6

PENTACHLOROBIPHENYL ADDED TO 12% STACK GAS UPSTREAM OF QUARTZ FILTER

TOTAL RESPONSE VS CONCENTRATION

ROW	1 (324)	2 (326)	3 (ug/m <sup>3</sup> )
1	456	329	0
2	476	366	0
3	485	371	0
4	490	383	0
5	1005	1075	4.921
6	919	993	4.921
7	945	1030	4.921
8	1313	1634	10.539
9	1241	1459	10.539
10	1261	1556	10.539
11	1986	2563	20.048
12	2091	2818	20.048
13	2222	3152	20.048
14	659	516	1.117
15	641	497	1.117
16	567	480	1.117
17	690	607	2.29
18	690	645	2.29
19	703	586	2.29

For column 2 versus column 2

Slope            0.6383  
 Intercept       284.073  
 Corr. Coef      0.997822

For column 1 versus column 3

Slope            78.4671  
 Intercept       509.44  
 Corr. Coef      0.993754

For column 2 versus column 3

Slope            122.334  
 Intercept       356.743  
 Corr. Coef      0.991083

M/Z	3s	Detection Limit
324	45.0	0.571 ug/m <sup>3</sup>
326	49.9	0.571 ug/m <sup>3</sup>

TABLE 8.7

HEXACHLOROBIPHENYL ADDED TO 12% STACK GAS UPSTREAM OF QUARTZ FILTER

TOTAL RESPONSE VS CONCENTRATION

ROW	1 (360)	2 (362)	3 ( $\mu\text{g}/\text{m}^3$ )
1	496	559	0
2	501	598	0
3	518	582	0
4	531	604	0
5	1078	1148	11.051
6	1135	1153	11.051
7	1050	1101	11.051
8	1518	1444	23.668
9	1273	1320	23.668
10	1333	1411	23.668
11	2313	2241	45.023
12	2613	2437	45.023
13	2779	2679	45.023
14	688	770	2.509
15	668	751	2.509
16	679	665	2.509
17	781	800	5.143
18	836	850	5.143
19	801	824	5.143

For column 1 versus column 2

Slope 1.09309  
 Intercept 125.686  
 Corr. Coef 0.998101

For column 1 versus column 3

Slope 43.4361  
 Intercept 536.992  
 Corr. Coef 0.982999

For column 2 versus column 3

Slope 39.7402  
 Intercept 606.202  
 Corr. Coef 0.984948

M/Z	3s	Detection Limit
360	48.2	1.109 $\mu\text{g}/\text{m}^3$
362	60.3	1.518 $\mu\text{g}/\text{m}^3$

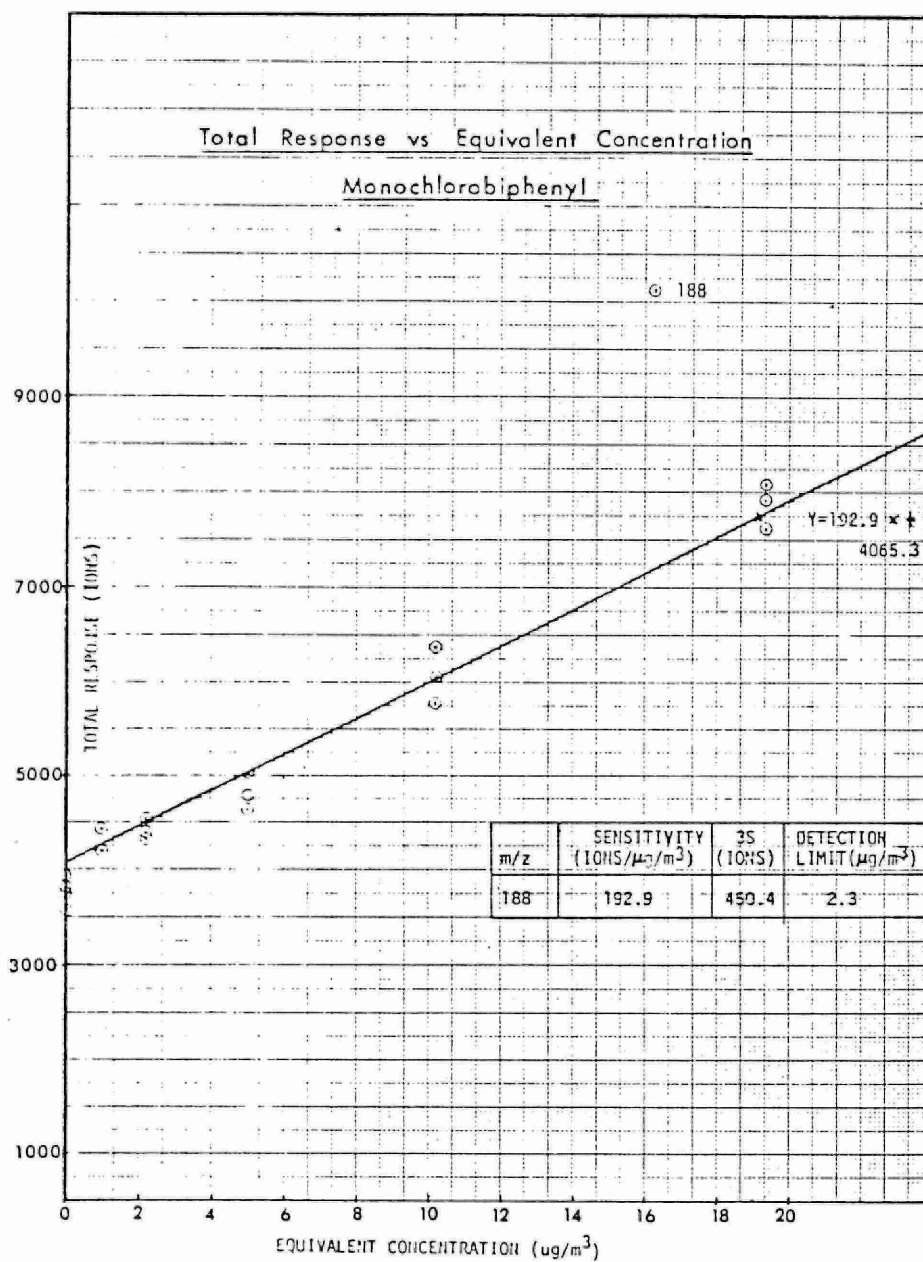
Figures 8.2, 8.3, 8.4, 8.5, 8.6 and 8.7 show in graphical form the total system's response to the injected PCB species (monochlorobiphenyl to hexachlorobiphenyl, inclusive). The two most abundant isotope peaks (except monochlorobiphenyl) were monitored for each PCB species containing an equal number of chlorine atoms. The detection limits of the instrument were determined from the curves for each PCB species. It is to be noted that the detection limit is defined as being  $3s$ , where  $s$  is the standard deviation calculated from the set of repeated measurements of the background signal taken before the injection of the known amounts of PCBs at each mass-to-charge position of interest. This has been given in detail in Chapter 4.

Table 8.8 summarizes the overall results. The figure also shows that the correlation coefficients between (a) the equivalent concentration and the total system's response are in the range of 0.928 - 0.996 and (b) the responses of the two most abundant isotopes of each PCB group is between 0.980 - 0.999. The tabulation also shows that deviation between the observed and theoretical or expected isotopic ratios are within 5 % except for the hexachloro species (11%). These correlations lead to an added confidence in distinguishing between a true PCB response and interfering background peaks. This can further be substantiated by the poor correlations (0.1 - 0.4) when PCBs are not added to the diluted gas stream (see Table 4.2).

In summary, the minimum detectability of the vaporized PCBs in the stack in micrograms per cubic meter with a signal-to-noise ratio of 3:1 are (this signal-to-noise ratio is quite stringent, during the test burn it will be possible to measure with a lower ratio):

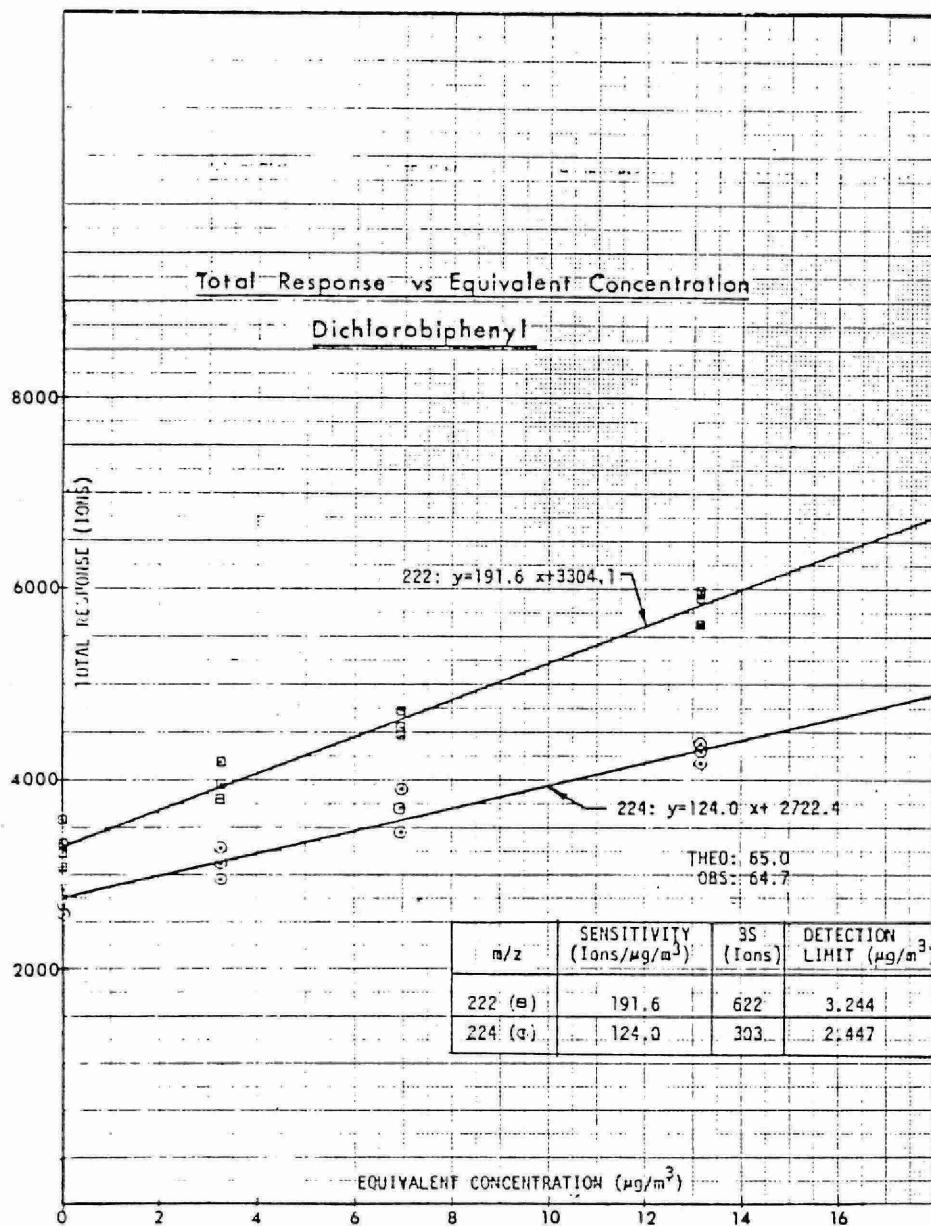
<u>PCB Species and Mass Peak</u>						<u>"Worst-Case" Minimum Detectability (sum of all species)</u>
Mono	Di	Tri	Tetra	Penta	Hexa	
<u>188</u>	<u>224</u>	<u>256</u>	<u>290</u>	<u>324</u>	<u>360</u>	
2.335	2.443	0.392	1.671	0.571	1.109	8.521

The "Worst-Case" minimum detection limits by the MOE TAGA<sup>TM</sup> have been observed to fluctuate on a day-to-day basis due to the changing



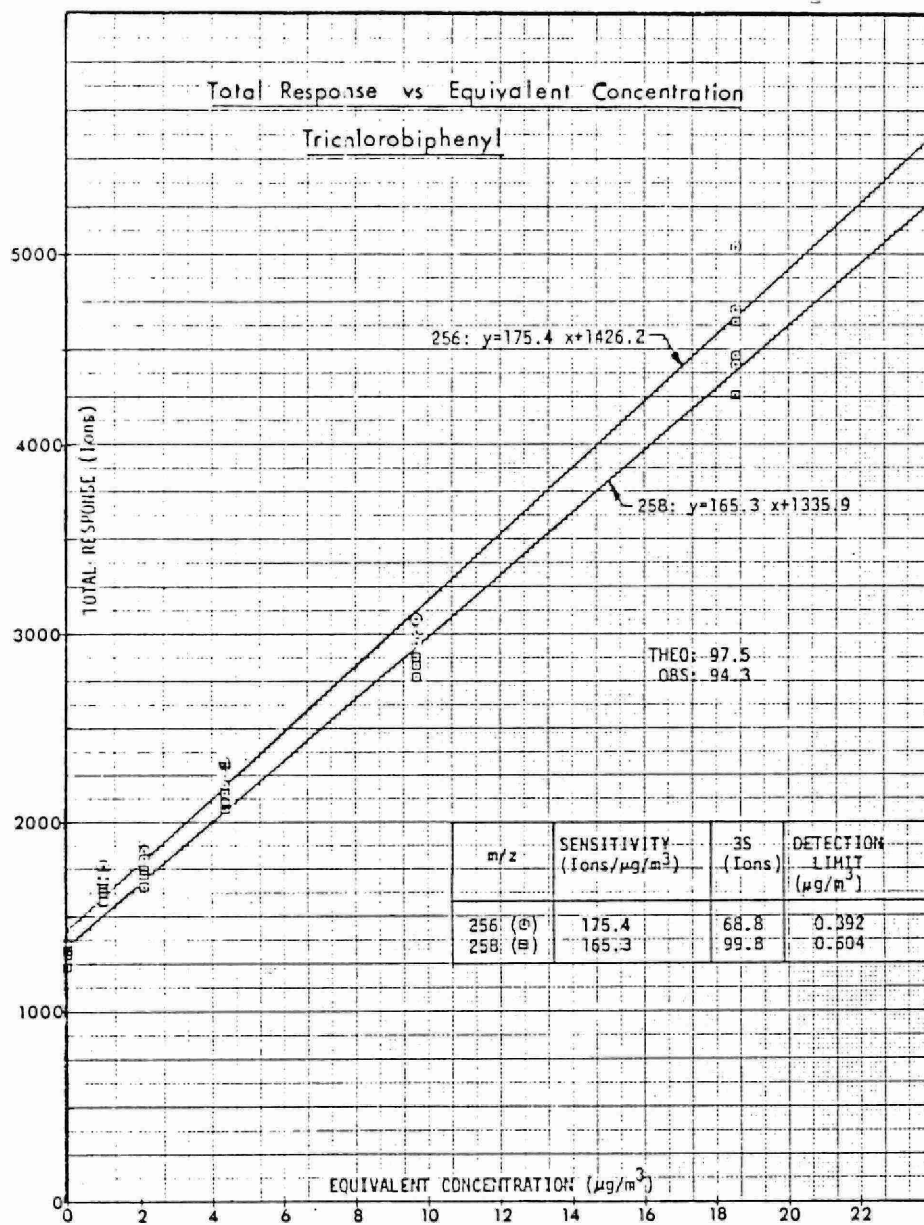
PCB ADDED IMMEDIATELY DOWNSTREAM OF KILN DUCT (UPSTREAM OF FILTER)  
(February 18, 1980)

Figure 8.2



PCB ADDED IMMEDIATELY DOWNSTREAM OF KILN DUCT (UPSTREAM OF FILTER)  
(February 18, 1980)

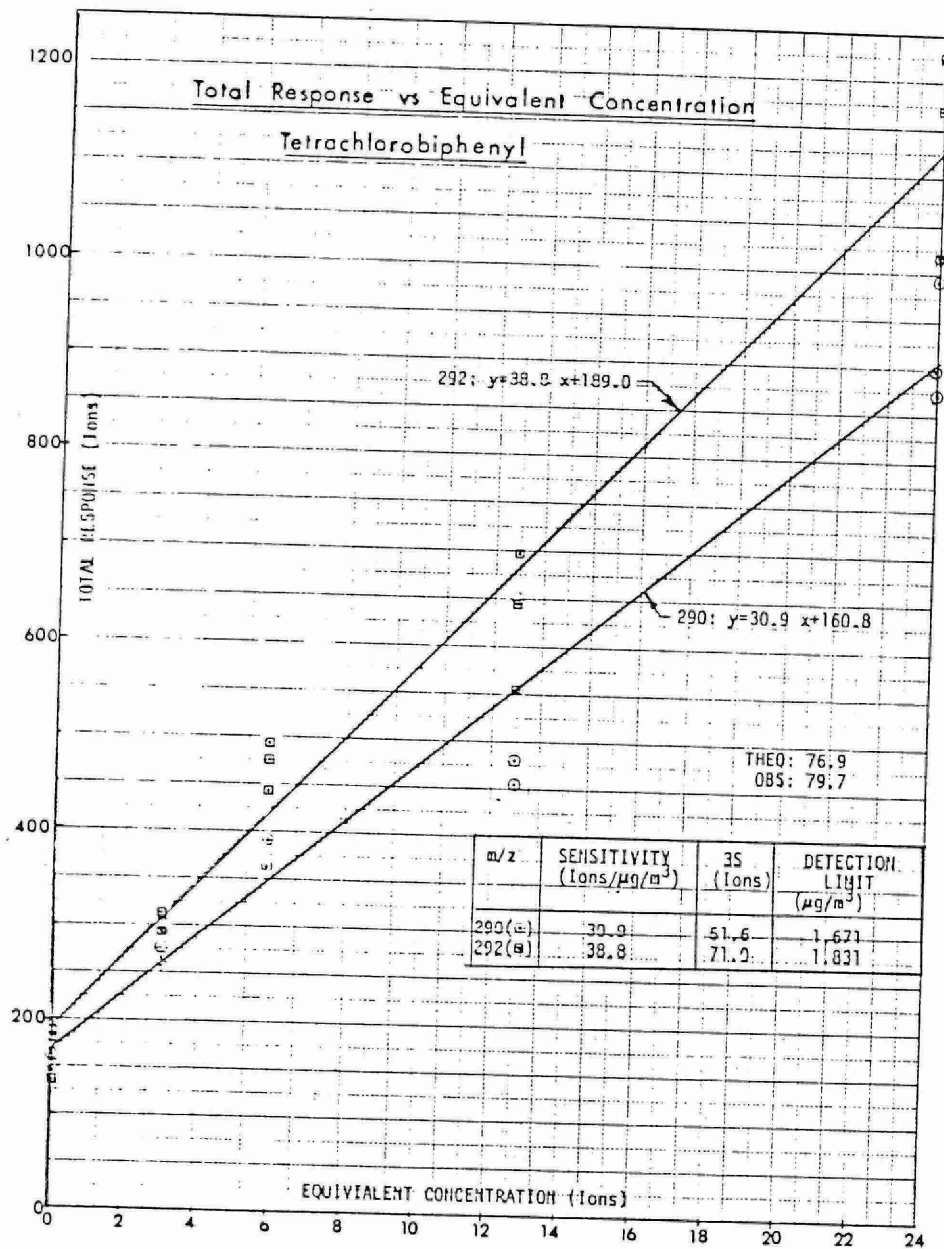
Figure 8.3



PCB ADDED IMMEDIATELY DOWNSTREAM OF KILN DUCT (UPSTREAM OF FILTER)  
(February 18, 1980)

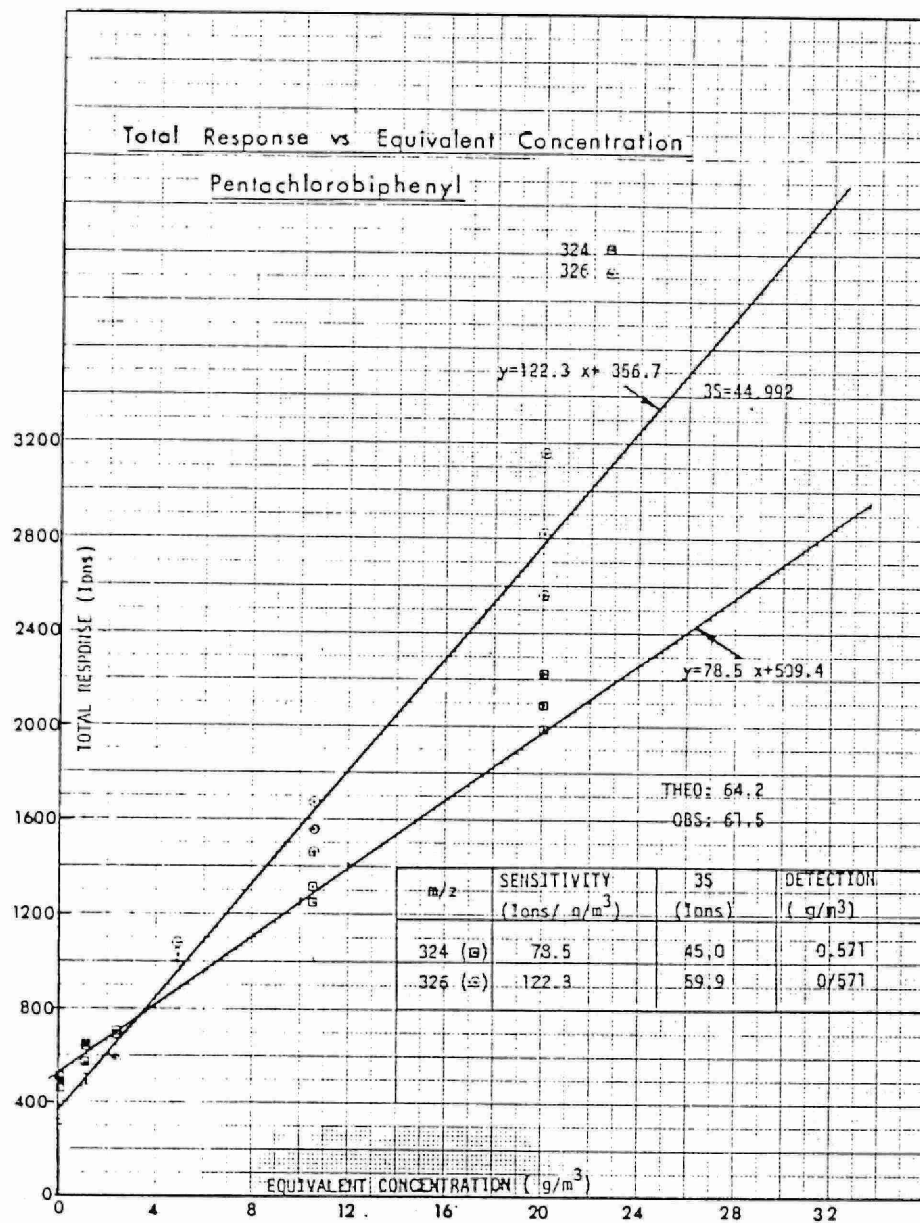
Figure 8.4





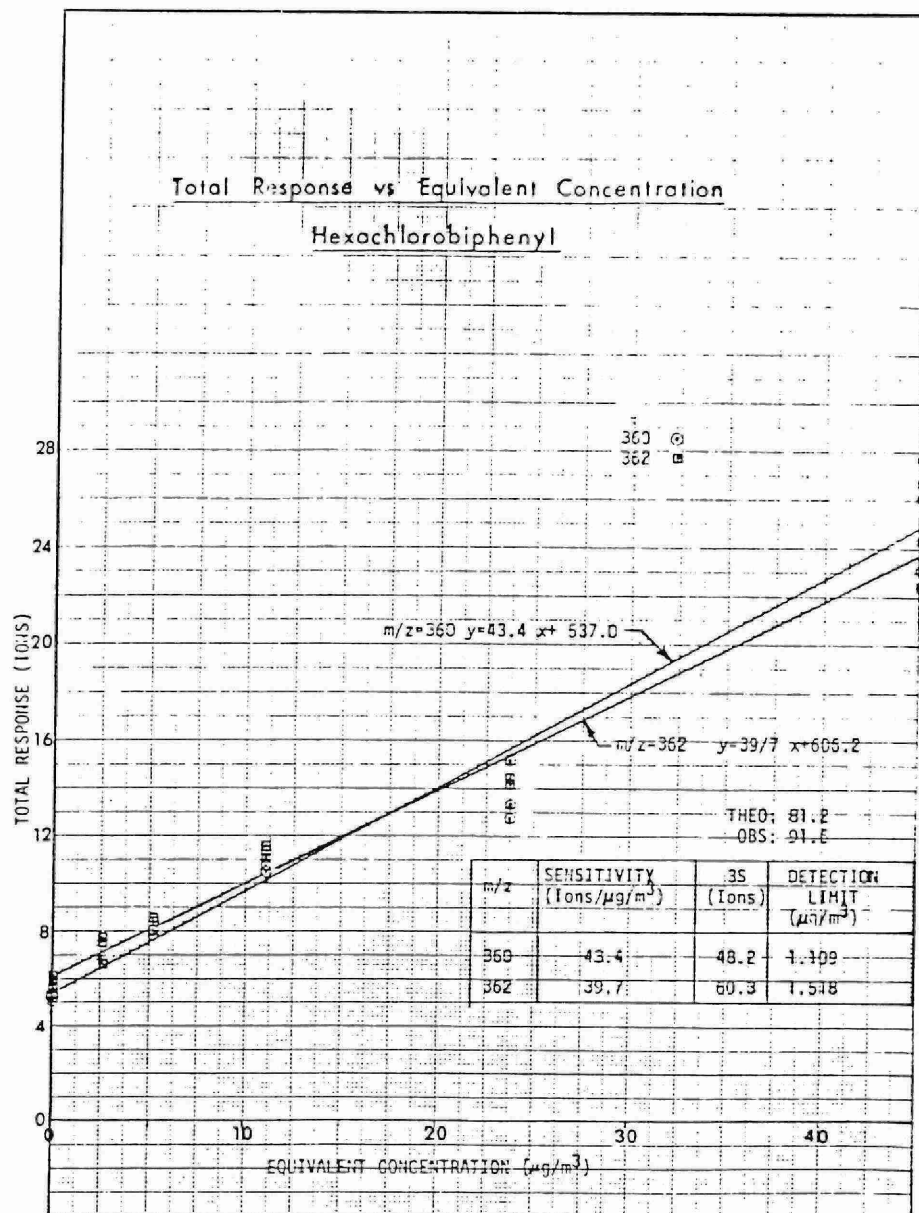
PCB ADDED IMMEDIATELY DOWNSTREAM OF KILN DUCT (UPSTREAM OF FILTER)  
(February 18, 1980)

Figure 8.5



PCB ADDED IMMEDIATELY DOWNSTREAM OF KILN DUCT (UPSTREAM OF FILTER)  
(February 18, 1980)

Figure 8.6



PCB ADDED IMMEDIATELY DOWNSTREAM OF KILN DUCT (UPSTREAM OF FILTER)  
(February 18, 1980)

Figure 8.7

and fluctuating background chemicals (other than PCBs) present in the stack gas and ambient air (used for dilution). None of these minimum detection limits exceeds the safety limit of 20 micrograms per cubic meter specified in the Test Burn Protocol (Ref. 5). These results indicate a need to establish the background levels of chemicals on a day-to-day basis during the test burn.

#### 8.4 PCB Budget Along the Sampling Line

In order to evaluate the PCB transfer efficiency throughout the sampling line, known amounts of Standard Solution #2 (See Table 3.6) were injected at all the three injection ports specified in Figure 7.18, i.e.,

IP 1: upstream of the quartz filter, immediately downstream of the duct,

IP 2: downstream of the quartz filter

IP 3: upstream of the TAGA<sup>TM</sup> 3000 unit.

A number of background readings for a 12% stack gas/88% heated ambient air mixture and responses to PCB injections were made at injections at IP 3 followed by IP 2 and then at IP 1. The total responses for all experiments were compared in order to derive the PCB transmission coefficients or PCB budget along the line.

Table 8.8 compares the total system's response when equal amounts of PCBs were injected at IP 1, IP 2 and IP 3 with the composite background. Table 8.9 shows the transmission efficiency throughout the system. To obtain the results in Table 8.9, the results in Table 8.8 were used. The results indicate that the sampling line transports the injected PCBs without any significant loss on the walls or the filter assembly and dust loading (roughly a 100% transmission for all tested PCB species).

TABLE 8.8

Comparison of Total Responses at Different Injection Points

Species	m/z	PCB Concn. (ug/m <sup>3</sup> )	Total Response Upstream (IP 2)		Total Response Downstream (IP 2)		Total Response Van (IP 3)		Background	
			Av of 3	s <sub>1</sub>	Av of 3	s <sub>2</sub>	Av of 3	s <sub>3</sub>	Av of 4	s <sub>4</sub>
Mono	188	1.924	6901	148	7532	242	6888	28	5634	21
Di	222	1.304	11871	149	13653	51	11443	224	8798	160
	224		10291	284	11652	137	9888	34	7794	221
Tri	256	1.840	1878	44	1734	82	1753	63	1042	72
	258		1838	104	1636	77	1756	66	1051	46
Tetra	290	2.379	1030	23	1110	35	1013	34	402	23
	292		1177	61	1320	18	1165	78	435	5
Penta	324	1.988	555	23	650	9	567	24	272	23
	326		589	57	687	21	623	43	206	11
Hexa	360	4.465	1159	59	1269	25	1235	29	566	28
	362		1211	42	1304	25	1223	25	671	24

TABLE 8.9

Total PCB Budgeting (% Transmission)

Species	m/z	Van (IP 3)	Downstream of Filter (IP 2)	Upstream of Filter (IP 1)
Mono	188	100 %	$109 \pm 12$ %	$100 \pm 7$ %
Di	222	100	$119 \pm 8$	$104 \pm 8$
	224	100	$117 \pm 12$	$104 \pm 11$
Tri	256	100	$99 \pm 11$	$107 \pm 10$
	258	100	$93 \pm 10$	$105 \pm 12$
Tetra	290	100	$109 \pm 7$	$102 \pm 3$
	292	100	$113 \pm 12$	$101 \pm 7$
Penta	324	100	$101 \pm 8$	$98 \pm 5$
	326	100	$110 \pm 7$	$95 \pm 9$
Hexa	360	100	$103 \pm 5$	$94 \pm 7$
	362	100	$106 \pm 5$	$99 \pm 5$

9.0

Mass SPECTRAL ANALYSIS OF STACK GAS

As mentioned in previous chapters a severe interference problem was experienced with the stack gas discharged from kiln #1 of St. Lawrence Cement, which had been slated for a PCB testburn. In order to understand the nature of this interference problem it was felt necessary to identify contaminants present in the stack gas.

A number of spectra had been collected and interpreted. A technical memorandum titled "Tentative Mass Spectral Identification of St. Lawrence Cement Stack Gas" has been prepared and is attached as an appendix, which describes the experiments and interpretations needed to solve this interference problem.

## References

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- (1) O. Hutzinger, S. Safe and V. Zitko: The Chemistry of PCBs. CRC Press, Cleveland, Ohio (1974)
- (2) W. Clark: "Much too hot not to handle" Maclean's, 92(51), pp. 40-42
- (3) H. L. Carey and R. P. Whalen, "Love Canal: Public Health Time Bomb - A Special Report to the Governor and Legislative" New York State of Department of Health, Albany, New York (1978)
- (4) L. P. MacDonald, D. J. Skinner, F. J. Hopton and G. H. Thomas "Burning Waste Chlorinated Hydrocarbons in a Cement Kiln", Technology Development Report EPS 4-WP-77-2 Water Pollution Contamination Directorate, Fisheries and Environment Canada, Ottawa (1977)
- (5) G. Van Volkenburgh "Protocol for the Incineration of Polychlorinated Biphenyls at St. Lawrence Cement Ltd. Mississauga" Air Resources Branch, Ministry of the Environment, Toronto, Ontario (1979)
- (6) "Development of Methodologies for the Analysis of Polychlorinated Biphenyls (PCBs) in Air Using the TAGA System" Final Report (1979-C) Prepared for Dr. E. Singer, Air Resources Branch, Ontario Ministry of the Environment SCIEX INC. Thornhill, Ontario (1979)
- (7) T. Sakuma, D. Robinson, W. K. Duholke and O Meresz", Application of Mass Spectrometry in Environmental Analysis: Defining Sources of Ground Water Pollution (Ref. 7-Cont'd) Presented at the 1976 CIC Conference, London, Ontario. June 7-9(1976)
- (8) SCIEX INC. "Operator's Manual - TAGA<sup>TM</sup>3000 TS300001" SCIEX INC. Thornhill, Ontario (1979)



- (9) L. Elias "Use of Vapour Trace Detection in Aircraft Security; Field Trials with TAGA2000 Mass Spectrometer" Laboratory Technical Report LTR-UA-44, National Research Council Canada, Ottawa, (1978)
- (10) J. A. Parsons, "Practical Mathematical and Statistical Techniques for Production Managers", Printice-Hall, Inc. Englewood Cliffs, N.J. (1973), p. 93
- (11) M. R. Spiegel "Schaum's Outline of Theory and Problems of Statistics" McGraw Hill, New York, N.Y. (1961)
- (12) F. W. McLafferty, "Interpretation of Mass Spectra" 2nd Edition, W. A. Benjamin, Inc. Reading, MA (1973)
- (13) R. C. Weast, Ed., Handbook of Chemistry and Physics, 55th Edition, CRC Press, Cleveland, Ohio (1974)
- (14) N.G.H. Guilford, "Design of Cyclone for Dust Removal from Ambient Air for SCIEEX Limited, APS 78-05" Report 78-01, Ontario Research Foundation, Mississauga, Ontario (1978)



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